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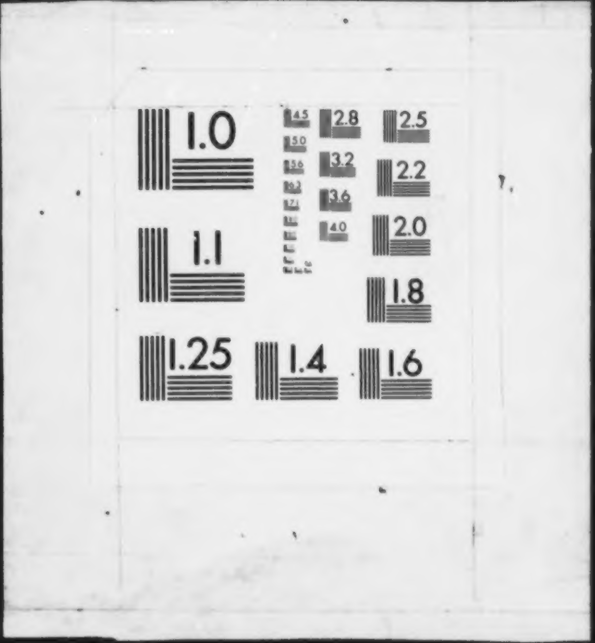
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Acurex Corp., Mountain View, CA

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Volume 2. Power Plant Integration, Economics, and Full-scale Experience

Symposium Cochairpersons:
M. W. McElroy (EPRI) and R. D. Stern (EPA)

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555 Clyde Avenue
Mountain View, CA 94039

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16. ABSTRACT The proceedings document the First Joint Symposium on Dry SO2 and Simultaneous SO2/NOx Control Technologies, held November 13-16, 1984, in San Diego, CA. The symposium, sponsored jointly by EPRI and EPA, was the first meeting of its kind devoted solely to the discussion of emissions control processes based on dry injection of calcium or sodium sorbents to meet SO2 and NOx regulations for coal-fired power plants. Processes that were discussed included: direct furnace injection of calcium-based sorbents, sorbent injection combined with low-NOx burners for simultaneous SO2/NOx control, and post-furnace injection of calcium and sodium sorbents. The symposium provided a timely forum for the exchange of data and information on the current status and plans for these emerging technologies. The presented papers began with a keynote address on acid rain strategies and control technology implications, followed by overviews of EPRI, EPA, and Canadian programs and the utility perspective for dry control technologies. Other papers focused on the latest advances in fundamental research and process design, power plant integration and economics, field applications, and full-scale testing. In addition to the U.S. and Canada, attendees represented West Germany, France, The Netherlands, Austria, and Japan.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Electric Power Plants	Pollution Control	13B	10B
Nitrogen Oxides	Coal	Stationary Sources	07B	21D
Sulfur Dioxide	Combustion	Dry SO_2 Control		21B
Sorbents	Economics	Simultaneous SO_2/NO_x Control	11G	05C
Calcium				
Sodium				

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ABSTRACT

Forty six papers describing recent advances in dry sorbent injection technologies for SO_2 control were presented at the 1st Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies. These papers covered the following topics: fundamental research; pilot-scale development of furnace injection; burners for simultaneous SO_2/NO_x control; post-furnace SO_2 removal; process integration and economics; sorbent availability and costs; and field applications and full-scale testing.

PREFACE

The 1st Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies was held November 13 through 16, 1984 in San Diego, California. This symposium, jointly sponsored by EPRI and EPA, was the first meeting of its kind devoted solely to the discussion of emissions control processes based on dry injection of calcium or sodium sorbents to meet SO_2 and NO_x regulations for coal-fired power plants. Specific processes that were discussed included: direct furnace injection of calcium-based sorbents, sorbent injection combined with low-NO_x burners for simultaneous SO_2/NO_x control, and post-furnace injection of calcium and sodium sorbents. The objective of the symposium was to provide a timely forum for the exchange of data and information on the current status and plans for these emerging technologies.

Forty six papers were presented beginning with a keynote address on acid rain strategies and control technology implications, followed by overviews of the EPRI, EPA, and Canadian programs, and the utility perspective for dry control technologies. Other papers focused on the latest advances in fundamental research and process design, power plant integration and economics, field applications, and full-scale testing. A panel of representatives from architect-engineering firms, boiler manufacturers, and utility companies discussed the impact of dry SO_2 control processes on new and existing power plants.

The speakers included EPRI and EPA staff members as well as representatives from utility companies, manufacturers of utility boilers and process equipment, sorbent suppliers, and research and development groups conducting investigations sponsored by EPRI, EPA, and others. Participants from West Germany, France, The Netherlands, Austria, Canada, and Japan provided a worldwide update on technological developments and an international perspective on SO_2 and SO_2/NO_x control issues.

The Cochairmen of the symposium were Michael W. McElroy, Subprogram Manager of EPRI's Air Quality Control Program in the Coal Combustion Systems Division and Richard D. Stern, Chief of EPA's LIMB Applications Branch of the Industrial Environmental Research Laboratory.* The welcoming address was given by John Hamrick, Vice President of Customer Service for San Diego Gas & Electric and the keynote address was given by Donald J. Ehreth, Deputy Assistant Administrator, Office of Research and Development, EPA.

The symposium proceedings has been published in two volumes:

- Volume 1: Fundamental Research and Process Development

  -- Session I: Introduction
  -- Session II: Fundamental Research
  -- Session III: Pilot-Scale Development of Furnace Injection
  -- Session IV: Burners for Simultaneous SO_2/NO_x Control
  -- Session V: Post-Furnace SO_2 Removal

(*) Now, the Air and Energy Engineering Research Laboratory.

- Volume 2: Power Plant Integration, Economics, and Full-Scale Experience

  -- Session VI: Process Integration and Economics
  -- Session VII: Sorbent Availability and Costs
  -- Session VIII: Field Applications and Full-Scale Testing

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SESSION VI: PROCESS INTEGRATION AND ECONOMICS

Chairman, David Lachapelle, EPA, IERL/RTP

FIRESIDE CONSEQUENCES OF FURNACE LIMESTONE INJECTION FOR SO_2 CAPTURE

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ABSTRACT

The influence of limestone injection on the furnace performance characteristics of two coals was investigated experimentally in Combustion Engineering's pilot scale Fireside Performance Test Facility (FPTF), under an EPRI sponsored study. The slagging, fouling and emission characteristics of a high sulfur, high iron Illinois #6 bituminous coal and a low sulfur, high sodium Montana subbituminous coal were investigated under low NO_x conditions. Calcium to sulfur ratios of 2-4 were investigated in detail.

Results indicate that limestone can be injected without adversely affecting the slagging and fouling performance of units firing these fuels. For high sodium coals it has significant potential for reducing fouling by weakening the deposit to tube bond, thereby enhancing sootblower cleaning effectiveness. With each coal upper limits for limestone dosage were established based upon either deposit accumulation and/or heat transfer rates.

INTRODUCTION

Furnace limestone injection in conjunction with low NO_x firing systems is under consideration as a way of reducing the costs of controlling SO_2 emissions from pulverized coal-fired power plants. In this process, limestone ($CaCO_3$) is injected into the furnace where it is calcined to lime (CaO). The lime reacts with SO_2 to form solid calcium sulfate particles which are removed from the flue gas in a conventional particulate control device. This dry, front-end process is attractive because of its potential lower capital cost and relative simplicity of design and operation, particularly for low and medium sulfur coals where only a modest amount of sulfur capture may be required.

Furnace limestone injection has been performed by numerous researchers in facilities ranging from small scale laboratory furnaces to utility steam generators. Wide ranges of sulfur capture have been reported with greater capture occurring in those combustors having lower temperatures and extended residence times. Earlier tests with high sulfur coals have reported SO_2 removal efficiencies in the range 17 50% during furnace limestone injection at a Ca/S ratio of two. (1,2,3).

A major unanswered question regarding furnace limestone injection is its impact on ash deposition in the radiant section (slagging) and convective passes (fouling) of a steam generator. Furnace limestone injection will increase the particle loading and change the chemical composition of the ash, and therefore influence the character of ash deposits in various sections of a steam generator. The distribution and quantity of these deposits and their chemical and physical properties have an important impact on heat transfer performance and steam generator performance. These factors, therefore, have a major bearing on the feasibility and cost of furnace limestone injection.

The ultimate objectives of this study were to (1) determine the effects of limestone injection under low NO_x firing conditions on the slagging and fouling behavior of two coals with ash characteristics representing generic slagging and fouling behavior encountered in the utility industry, and (2) interpret these effects as they relate to boiler operation and performance.

The ash behavior was evaluated using the Fireside Performance Test Facility (FPTF), a pilot scale combustion test facility designed to simulate the radiant and convective heat transfer surfaces, ash properties and combustion conditions in a pulverized coal-fired boiler (4). Test results from this facility have shown excellent agreement with field slagging and fouling performance (5).

TEST PROGRAM

To attain the project objectives, Combustion Engineering, under an EPRI contract performed a two phase pilot scale study. The first phase involved furnace studies on a moderate ash, high sulfur, high iron, Midwestern Illinois #6 high volatile C bituminous coal. The second phase involved furnace studies on a low ash, low sulfur, high sodium, Montana subbituminous B coal. Both coals are burned commercially in utility boilers and were selected for their differing slagging and fouling characteristics. Experience with the Illinois #6 coal indicates that it exhibits high slagging and moderate fouling tendencies while high slagging and high fouling tendencies are characteristic of the Montana subbituminous coal under standard firing conditions. The limestone used during both phases of testing was Marblewhite 200 obtained from Pfizer Chemical, Inc. The two coal and limestone analyses are included in Table 1. The coals were pulverized to a fineness of 75-80% less than 200 mesh and the limestone was typically 96% less than 200 mesh.

Illinois #6 coal testing included a series of short term NO_x optimization tests, a series of short term SO_2 optimization tests, and nine long term (40 continuous hours) tests evaluating slagging and fouling. The short term tests were performed to establish firing conditions for long term slagging and fouling testing. Long term tests were performed at conditions simulating full and reduced load boiler operation. Their 40 hour duration has been established based on past experience relating FPTF deposits with those from the field. Standard firing, low NO_x (baseline) and low NO_x with limestone addition tests were run to evaluate the effects of low NO_x firing and limestone addition during low NO_x firing, individually. Long term limestone injection tests were performed at Ca/S mole ratios of 2.0 and 3.5.

Phase II testing with the Montana coal included a series of short term NO_x, SO_2 optimization tests and four long term tests (40 hour) evaluating slagging and fouling. The short term tests were performed to establish firing conditions for long term testing. The four long term tests were run at constant low NO_x firing conditions simulating full load boiler operation. During the long term tests only Ca/S mole ratios were varied. Ca/S mole ratios of 0 (baseline), 1.0, 2.0, and 4.0 were investigated.

The primary objective of this work was to evaluate the slagging and fouling consequences of furnace limestone injection under representative SO_2 removal conditions. Furnace limestone injection geometry and operating conditions were not selected to optimize SO_2 capture. Sulfur capture levels observed in the FPTF were in the range of previous field experience.

TEST FACILITIES AND PROCEDURES

The ash behavior of the fuels was evaluated using the Fireside Performance Test Facility (FPTF) (Figure 1), a pilot scale (2-4 MMBTU/hr 0.6-1.2 MW) combustion test facility designed to simulate the heat transfer surfaces, combustion conditions and ash deposit properties in a pulverized coal fired boiler. The FPTF furnace is bottom fired with staged combustion capabilities to simulate a low NO_X combustion environment. The furnace radiant section, designed to simulate the temperatures and residence times of a full scale boiler, contains a simulated waterwall test surface to evaluate lower furnace ash deposition. In the convective section, designed to simulate velocities and a range of temperatures corresponding to a full scale boiler, four banks of air cooled probes are used to simulate boiler reheater and superheater tubes and study convective section ash deposition. Short term test results led to the injection of overfire air through the middle location to reduce NO_X emissions and limestone through the side location for all long term tests (10). Temperature conditions associated with low NO_X firing were believed to be essential for SO_2 removal at the beginning of this project.

Lower furnace ash deposition (slagging) is evaluated based upon the waterwall panel deposit cleanability (evaluated using an air lance which simulates commercial sootblowing conditions), physical characteristics and the impact of the deposit on waterwall panel heat flux. Convective section ash deposition (fouling) is evaluated based upon the convective ash deposit physical characteristics, accumulation and cleanability. Cleanability is evaluated with a force meter to determine deposit to tube bonding strength measurements (BSM's); BSM's ≤ 15 indicate deposits are controllable with conventional sootblowers.

The flue gas SO_2 concentration is measured downstream of the FPTF convective section. A gas sample is drawn into a phase discriminating probe which separates the suspended flyash particles from the gas sample and quenches (200°F, 93°C) the gas sample to prevent further SO_2 - alkali reactions. The gas sample is not cooled below the sample dew point because any water present would absorb SO_2. The SO_2 measurement is performed by a Dupont SO_2 analyzer. Flue gas NO_X concentration is also measured downstream of the FPTF convective section, using a second gas sample line. The gas sample is conditioned to remove flyash particles and water vapor, then introduced into the gas analysis system. A chemiluminescent analyzer measures the NO_X concentration. Other analyzers measure the concentrations of CO, CO_2, and O_2.

SLAGGING CHARACTERISTICS OF ILLINOIS # 6 COAL

Baseline Results

During standard firing (20% excess air, no overfire air) of Illinois #6 coal the "critical" temperature range for controlling lower furnace ash deposits was 2900-3000°F (1593-1649°C). In this range waterwall panel deposits changed from sintered (1/4-1/2 inch, 0.6-1.3 cm thick) and cleanable through sootblowing to molten (1/2-3/4 inches, 1.3 - 1.9 cm thick). Deposit physical states are very similar between the FPTF and the field; generally field deposits are a bit thicker than those generated in the FPTF. Deposits on utility waterwalls are also sintered to molten in nature, 0-4 inches (0-10 cm) thick at comparable furnace conditions. Although the field deposits are controllable with regular sootblowing, this change in physical state (from sintered to molten) plus experience at the utilities indicates that there is little margin to increase load (temperature) beyond this point. Hence this 2900-3000°F (1593-1649°C) range can be considered a critical temperature for both the FPTF and the field.

Effect of Staged Combustion

Low NO$_x$ or reducing conditions had a pronounced effect on increasing the severity of slagging with this high iron coal. In Figure 2 waterwall panel heat flux is shown for tests with (Test B, primary stage stoichiometry of 0.9) and without (Test A, primary stage stoichiometry of 1.2) staged combustion. Flame temperatures during both tests were similar (2620-2630°F, 1438-1443°C); all tests were run with 20% overall excess air. Lightly sintered deposits covering about 50% of the lower panel and 40% of the upper panel developed during standard firing. The lower panel deposit was cleanable through sootblowing with heat flux increasing from 13,000 to 54,000 Btu/hr ft^2 (41-170 Kw/m^2) after sootblowing 12 hours into the test. In comparison, during low NO$_x$ firing molten deposits covering 100% of the lower panel and about 80% of the upper panel surface developed. After 12 hours of test firing the lower waterwall panel heat flux was approximately 22,000 Btu/hr-ft^2 (69 kw/m^2). The heat flux after sootblowing returned to between 25,000 and 30,000 BTU/hr-ft^2 (79-95 kw/m^2) indicating the molten deposits were not removed from the panel and were not controllable by sootblowing.

These results clearly show that staged combustion alone will have a pronounced effect on increasing slagging. Critical temperatures for slagging were greater than 2900°F (1593°C) for a primary stage stoichiometry of 1.2 and less than 2620°F (1438°C) for a primary stage stoichiometry of 0.9. The most likely cause of this is the fact that iron in a more reduced state melts at lower temperatures. Iron can also act to flux silica present in the panel deposit further lowering the melting temperature (6). Illinois #6 coal ash has about 14% iron (analyzed as Fe_2O_3). The iron has a strong influence on the slagging characteristics of the coal.

Effect of Limestone Addition Under Low NO$_x$ Conditions

Limestone addition at Ca/S mole ratios >2.0, during low NO$_x$ firing at flame temperature of 2600-2700°F (1427-1482°C) resulted in an overall improvement in slagging. Although waterwall panel deposits developed at a faster rate and increased thickness due to limestone addition, the deposit physical state and cleanability was generally improved.

Comparison of tests with Ca/S ratios of 0, 2.0, and 3.5 (Tests B, C, D, Figure 3) indicate poor deposit cleanability without limestone and good cleanability with limestone, evidenced by the sharp increase in heat flux immediately after sootblowing with limestone addition (17,000 to 73,000 Btu/hr ft^2 (54-230 kw/m^2) for test C, 15,000 to 60,000 Btu/hr ft^2 (47-189 kw/m^2) for test D.). Deposit physical state was molten at Ca/S of 0 and 2.0 and sintered at Ca/S=3.5. Panel surface coverage was 90-100% for all cases. However deposit accumulation was greater with increased limestone addition and the heat transfer benefits of improved cleanability were shortlived (5-6 hrs for Ca/S = 2.0, 2-4 hrs for Ca/S = 3.5). While this cleanable situation is still preferable to the baseline non-cleanable situation, conventional sootblowing frequencies on the order of 8 hours will not keep up with the increased accumulation rate for Ca/S = 3.5. Furthermore, the increased ash loading in this situation (26.5 lb/MMBTU vs. 9.2 lb/MMBTU for baseline, 48 vs

17 mg/kcal) is impractical from a material handling standpoint. A Ca/S ratio of less than two appears to be a practical upper limit for most high sulfur (3.5% S) coals based on the additional particulate loading due to limestone addition.

Results of baseline and limestone addition tests indicate that the addition of limestone resulted in a slight reduction in heat flux before blowing the panel due to the insulating effect of the deposit. Deposit thickness also increased with limestone feed rate, ranging from 1/8-1/4 inch (0.3-0.6 cm) at Ca/S=0 and 2.0 to 1/2-3/4 inch (1.3-1.9 cm) at Ca/S=3.5. However, the improvement in deposit cleanability with limestone addition resulted in an overall improvement in average waterwall panel heat transfer compared to the baseline (no limestone) test. These results indicate that during low NO_x steam generator operation with limestone addition, sootblowing will be required more frequently in the lower furnace. However, the blowers will be more effective in removing wall deposits with limestone addition.

FOULING CHARACTERISTICS OF ILLINOIS # 6 COAL

Baseline Results

During baseline standard firing and low NO_x firing Illinois #6 coal exhibited a moderate/low fouling potential. Above 2150°F (1177°C) highly sintered deposits developed during baseline tests. This shows excellent agreement with utility operation where highly sintered deposits develop above 2100°F (1149°C) on boiler heat transfer surfaces. Deposit accumulation was low for baseline tests with no accumulation below 1750°F (954°C) gas temperature. This temperature is between the normal operating gas temperatures for a finishing reheater and finishing superheater in a utility boiler.

Throughout Illinois #6 coal testing the convective probe deposit to tube bonding strengths were low ($\lesssim 5$). This result indicates that sootblowing should be effective at removing convective pass deposits during utility operation at standard, low NO_x or low NO_x with limestone injection firing conditions. Of key concern was deposit accumulation rate, measured during the final 8 hours of the FPTF tests.

For all baseline tests (both standard and low NO_x without limestone) deposit buildup rates were universally low (less than 0.3 lb/hr ft^2, 0.4 g/sec m^2) for gas temperatures below 2150°F (1177°C, Figure 4). Test F results also show that at gas temperatures above 2150°F (1177°C) deposit buildup rate significantly increased. At a gas temperature of 2300°F (1260°C) the deposit buildup rate increased to 1.1 lb/hr ft^2 (1.5 g/sec m^2).

The similar convective pass fouling results obtained during both the high NO_x and low NO_x FPTF tests indicated that changes in burner zone stoichiometry and/or flame temperature had little effect on the fouling characteristics of Illinois #6 coal. These results suggest that convective pass fouling deposit characteristics during utility operation employing a low NO_x firing system will be similar to fouling deposit characteristics obtained with the present firing systems.

Effect of Limestone Addition Under Low NO_x Conditions

Convective section probe deposit buildup rates increased significantly as limestone addition was increased from 0 to 2.0 to 3.5 during low NO_x firing with Illinois #6 coal. Convective pass deposit buildup rate curves for high firing rate tests E (Ca/S=0) and G (Ca/S=2) and low firing rate Tests B (Ca/S=0) H (Ca/S=2) and I (Ca/S=3.5) are presented in Figure 5. At both firing rates the effect of limestone addition on deposit buildup rate is evident. Both graphs show the considerable increase in deposit buildup rate that occurred due to limestone addition

(Ca/S = 2.0) in comparison with the baseline (Ca/S=0) curves. The low firing rate graph also shows that as limestone addition is increased from a Ca/S ratio of 2.0 to a Ca/S ratio of 3.5, there is a further substantial increase in deposit buildup rate.

The increase in deposit buildup rates, due to limestone addition, resulted in more frequent convective pass sootblowing cycles to maintain a standard deposit thickness of less than 3½ inches. During high firing rate baseline Test E and limestone addition Test G (Ca/S=2.0) the sootblowing frequency was about 15 hours and 5 hours respectively. Similar results were obtained during low firing rates Tests B, H, and I. Increasing the limestone feed rate from a Ca/S=0 to Ca/S=2.0 to Ca/S=3.5 increased the sootblowing frequency from 20 hours to 8 hours to 6 hours. Convective pass velocities during the high firing rate tests fell within the range of utility convective pass velocities for Illinois No. 6 coal. As a result the high firing rate deposit buildup rates best represent utility operation and indicate a Ca/S ratio of less than two is probably a practical upper limit based on sootblowing frequency (5 hours).

Deposit to tube bonding strength measurements (BSM's) were low during all tests, being slightly lower during limestone addition test (maximum less than 4, majority less than 1) than tests without limestone (maximum less than 4, majority of 1-3). As stated earlier deposit accumulation rate will be a limiting factor, limiting limestone addition to a Ca/S ratio of less than two with this coal.

Illinois #6 Coal SO_2 Capture Results

While not a primary objective of this project, results indicate that gas temperature and residence time have a strong influence on sulfur capture, with increased absorption occurring at extended residence times below 2300°F (1260°C). Earlier work performed by Battelle (7, 8) suggests the existence of an upper temperature limit (2300°F, 1260°C) for sulfur capture dictated by calcium sulfate thermodynamics. Therefore thermodynamics favor low temperatures.

The Battelle work also suggests a lower temperature limit for SO_2 absorption. The minimum temperature for SO_2 capture is less easily defined. Hence a "temperature window" may exist for SO_2 capture. The upper limit of this window is set by thermodynamics of calcium sulfate stability and is about 2300°F; the lower limit is established by lime/SO_2/O_2 reaction rates to form calcium sulfate and is unknown.

Data from the FPTF was correlated with temperature. Results correlated best with temperatures between 2300°F (1260°C) and 1800°F (982°C, typical FPTF convective section outlet temperature). Figure 6 supports the existence of an 1800-2300°F (982-1260°C) temperature window with SO_2 removal increasing with residence time in this window. At a residence time of about 0.7 seconds, which closely simulates residence time in a utility boiler in this temperature regime, about 25% sulfur capture was obtained at Ca/S=2.0.

SLAGGING CHARACTERISTICS OF MONTANA SUBBITUMINOUS COAL

Baseline Low NO_x Results

One limestone-free low NO_x test was performed as a basis for comparison with the limestone additive tests. During baseline Test A the average peak flame temperature was 2730°F (1499°C). One eighth to 1/4 inch (0.3-0.6 cm) thick molten deposits developed on the lower waterwall panel and 1/4 to 1/2 inch (0.6-1.3 cm) thick molten deposits developed on the upper waterwall panel. The deposits were fluid in nature, flowing down the panel surface. The lower and upper panel deposits were removed with the sootblower after 12 and 20 hours of testing (Test A, Figure 7). Very thin molten deposits may be removed from waterwall panel surfaces by thermally shocking the deposit with a relatively cold cleaning medium.

Utility boilers firing this high sodium Montana coal experience a similar slagging situation as was obtained during FPTF Test A. Thin molten deposits are generally obtained which do not significantly reduce heat transfer. Removal of these deposits through conventional sootblowing techniques, while not as effective as with dry or sintered deposits, is generally attained due to the fact that deposits are thin enough to permit thermal shocking.

Effect of Limestone Addition Under Low NO_x Conditions

Three long term tests were performed to evaluate the effect of limestone addition, during low NO_x firing, on the slagging and fouling behavior of this coal. Test conditions were consistent with Test A with the exception of limestone addition. Tests B, C, and D were performed at Ca/S ratios of 2.0, 1.0, and 4.0 respectively.

Results indicate that as limestone addition (Ca/S ratio) increased, waterwall panel deposit thicknesses increased and deposits became drier. At Ca/S ratios $\geq$2.0 thicker (1/4 to 1-1/4 inches, 0.6-3.2 cm) drier (sintered) deposits developed on both the lower and upper panels in comparison with the thin (1/8-1/4 inch, 0.3-0.6cm) molten deposits encountered during test A. At a Ca/S ratio of 1.0 (Test C), the lower panel deposit was similar to that from Test A. However, the Test C upper panel deposit was drier and thicker than from Test A. During limestone addition the formation of thicker sintered deposits on both the upper and lower panels restricted heat transfer in comparison with the baseline results. Sintered deposits generally have lower thermal conductivities than molten deposits. Hence the formation of thicker sintered deposits compounds the insulating effect. At Ca/S ratios$\geq$2.0 both upper and lower panel deposits resulted in a significant reduction in heat transfer to the panel compared to baseline results (Figure 7). The baseline steady state heat flux for the lower panel was about 45,000 BTU/hr ft^2 (142 kw/m^2) and for the upper panel about 20,000 BTU/hr ft^2 (63 kw/m^2). In comparison the test B (Ca/S=2) heat flux for the lower panel was 15,000 BTU/hr ft^2 (47 kw/m^2) and for the upper panel about 8000 BTU/hr ft^2 (25 kw/m^2), significantly lower due to the 1/4-3/4 inch (0.6-1.9 cm) sintered deposits which formed on the panel surface. Similarly, the Test D (Ca/S=4.0) lower panel steady state heat flux was approximately 13,000 Btu/hr ft^2 (41 kw/m^2) and the upper panel 8000 Btu/hr ft^2 (25 kw/m^2) with 1/2-1 1/4 inch (1.3-3.2 cm) sintered deposits.

At the 12 and 20 hour point of each test, the upper and lower panel deposit cleanabilities were evaluated with the sootblower. In general the deposits from each test were removed from the waterwall panel with the sootblower. The heat flux benefit from cleaning the waterwall panel varied from 1 to 5 hours before returning to a steady state condition. At Ca/S ratios$\leq$2.0 the lower panel heat flux recovery approached clean panel conditions (60,000 Btu/hr ft^2, 189 kw/m^2). At a Ca/S ratio of 4.0 (Test D), the lower panel recovery was less (35,000-45,000 Btu/hr ft^2, 110-142 kw/m^2) due to the greater rate of deposit accumulation and thicker deposits associated with the greater limestone feed rate.

During baseline low NO_x testing with this high sodium coal thin molten deposits developed on the waterwall panel. Sootblowing was effective at removing the deposits, due to a thermal shock mechanism. These results are consistent with utility operation with this coal at standard firing conditions. Limestone addition in the FPTF at Ca/S ratios $\geq$ 2.0 resulted in the formation of thicker sintered deposits, also amenable to sootblowing, but reduced heat transfer to the panel by greater than a factor of two. In a utility the reduction in heat transfer may be the limiting factor in establishing limestone additive feed rate. A possible alternative to obviate the reduced heat transfer effect is to add the limestone as high in the furnace as possible providing the limestone can be properly distributed. Given this scenario it may be possible to add limestone at Ca/S ratio >2.0.

FOULING CHARACTERISTICS OF MONTANA SUBBITUMINOUS COAL

Baseline Results

The fouling mechanism of the high sodium (6.9% Na_2O in ash, 4.9% ash) Montana Subbituminous coal studied is dominated by the active organic sodium compounds present in the coal (9). At furnace flame temperature these low melting sodium compounds vaporize. Condensation and solidification of the sodium compounds on relatively cold heat transfer surfaces and ash particles results in highly fused deposits which are tightly bonded to tube surfaces. The sodium compounds are therefore the "glue" responsible for formation of the strongly bonded deposits. Utility steam generators firing high sodium Montana subbituminous coal have experienced severe fouling problems. The buildup of strongly bonded deposits on reheater and superheater finishing sections (especially the areas not directly covered by sootblowers) has lead to pluggage and heat transfer problems. Constant cycling of the convective section sootblowers is required during boiler operation.

During low NO_x baseline Test A this coal exhibited a high fouling potential. The deposit buildup rate was relatively low with 3-1/2 inch (9cm) deposits developing on Probe Bank I after about 16 hours of furnace operation. However, the deposit to tube bonding strengths were high. Bonding strength measurements below 15 usually indicate the deposits will be controllable with conventional sootblowers. During baseline Test A average maximum bonding strength measurements fell in the 20-30 range indicating that at flame temperatures of about 2750°F (1510°C) and gas temperatures above 1920°F (1049°C) deposit cleanability is poor.

The physical state of the outer deposits ranged from hard/sintered on the front probes in Banks I and II (gas temperatures between 2085 and 2000°F (1140-1093°C)) to lightly sintered on the back probes in each section. The lightly sintered deposits were friable and broke into smaller pieces when contacted with the bonding strength apparatus. The hard, sintered deposits were difficult to break into smaller pieces when hit with an iron rod. These hard sintered deposits represent a problematic situation in a utility boiler. Not only are they difficult to remove from tube surfaces, once removed they are difficult to break into smaller pieces which may lead to pluggage of heat transfer surfaces downstream in a boiler, for example the economizer section.

Effect of Limestone Addition Under Low No_x Conditions

During the four low NO_x tests only Ca/S mole ratio was varied. Tests A, B, C, and D were performed at Ca/S mole ratios of 0, 2.0, 1.0, and 4.0 respectively. Results show that as furnace limestone addition increased, convective pass deposit buildup rates increased and deposit to tube bonding strengths decreased.

The most significant result of limestone addition, with regard to fouling, was the reduction of deposit to tube bonding strength measurements. Figure 8 presents the average bonding strength measurements obtained on probe Bank I (2100°F or 1149°C) for the four tests. In comparison with the baseline (Ca/S=0) average bonding strength of 30, at a Ca/S ratio of 1.0 (Test C) the average bonding strength value decreased to 7 as a result of limestone addition. Increasing the limestone addition rate to 2.0 and 4.0 resulted in further reductions in the bonding strengths of deposits. This trend was consistent throughout the FPTF convective section over the temperature range 2100-1700°F (1149-927°C). Therefore, the addition of limestone at Ca/S ratios >1.0 results in an improvement from a severe/high fouling situation to a moderate situation with deposits controllable with conventional sootblowers. Limestone addition also resulted in an improvement in the physical state of the deposits. As Ca/S ratio was increased the friability of superheater probe outer deposits tended to increase. This increased friability may reduce the potential for pluggage of boiler heat transfer surfaces with large deposits suspended in the gas stream.

Convective pass deposit accumulation rates (Figure 9) increased with limestone addition. As the Ca/S ratio increased from 0 to 1.0 to 2.0 to 4.0, sootblowing frequency increased from once every 16 hours to 11 hours to 8 hours to 6 hours respectively. These results indicate that a utility boiler should be able to operate at a Ca/S ratio between 2 and 4. However increasing the limestone additive feed rate above a Ca/S ratio of 4.0 will probably increase the convective pass sootblowing frequency to an impractical level, i.e., more than once per shift.

With respect to steam generator operation, the reduction in convective pass deposit to tube bonding strengths as a result of furnace limestone addition should be a great benefit. A high fouling situation (Ca/S=0) should be improved to a moderate situation (Ca/S >1.0) with deposits controllable with conventional sootblowers. Deposit buildup rates will increase as a function of limestone additive feedrate. A Ca/S ratio of between 2.0 and 4.0 appears to be an upper practical limit based on sootblowing frequency results in the FPTF.

Montana Subbituminous Coal SO_2 Capture Results

In comparison with Illinois #6 coal, the Montana subbituminous coal selected for the test program has about one-fifth the sulfur content and a significantly greater concentration of alkali in the ash (see Table 1). The alkali can react with SO_2 formed from the sulfur in coal to reduce flue gas SO_2 concentration significantly. The alkali/S mole ratio in this coal is 1.96, compared to 0.13 in Illinois #6 coal. As a result, the SO_2 absorption values obtained during testing are based upon a theoretical SO_2 emission value rather than a measured baseline SO_2 value as was the practice during Illinois #6 coal testing. The theoretical SO_2 value (457 ppm) was calculated based upon the ASTM ultimate analysis of a composite coal feed sample obtained from each long term test (0.5% sulfur).

Again results (Figure 10) indicate that sulfur capture was strongly influenced by Ca/S ratio and residence time between 1800-2300°F (982-1260°C). Sulfur capture increased from 2% to 35% as Ca/S ratios (based on limestone addition) increased from 0 to 5 at 0.4 second residence time and from 32% to 67% at 0.9 second residence time at similar Ca/S ratios. The 0.9 seconds results also indicate a substantial amount of sulfur capture (32%) by alkali in the coal ash. These results were obtained with minimal ash deposits.

A substantial amount of sulfur capture was also obtained by convection pass ash deposits with this coal. Results (Table 2) indicate that for similar residence times and Ca/S ratios sulfur capture increased by as much as 125 ppm for this coal. Given the low sulfur content of this coal this translated into as much as a 27% increase (31% to 58%) in sulfur capture.

UTILITY APPLICATON OF RESULTS

Illinois #6 Coal

Figure 11 is a schematic of a typical utility firing Illinois #6 coal at a standard firing condition with no limestone addition. The radiant and convective section problem areas are indicated. While utility boilers firing Illinois #6 coal generally have not experienced major slagging problems, FPTF results suggest they are operating at a critical temperature (2900-3000°F)(1590-1650°C) with little, if any, safety margin. An increase in flame temperature may lead to slagging problems. Extensive fouling of the reheater pendant and economizer surfaces has been experienced in some utilities firing Illinois #6 coal. The buildup of hard sintered deposits on closely spaced reheater elements results in deposit bridging between tubes, requiring frequent sootblowing. Hard sintered deposits that are removed by sootblowing convective surfaces lodge in the straight finned staggered tube economizer resulting in economizer pluggage. Frequent sootblowing and/or pluggage of heat transfer surfaces leads to erosion of tube surfaces and accelerates tube failure.

Figure 12 is a schematic of a utility firing Illinois #6 coal with a low NO_x firing system and furnace limestone injection (Ca/S=2.0). Assuming that a low NO_x firing system can be designed and implemented without increasing slagging, then limestone addition at a Ca/S ratio $>$ 2.0 will reduce slagging. Accumulation of waterwall deposits will increase, requiring more frequent sootblowing, but cleaning effectiveness will also increase. A greater number of sootblowers and more frequent blowing will be required in the pendant reheater area. Limestone feed rate will ultimately be limited by the ability of the sootblowers to keep up with deposit accumulation in the pendant reheater and will most likely be limited to Ca/S $\lesssim$2. Bare tube in-line economizers are recommended, if possible, to reduce pluggage of economizer sections due to the lodgement of deposits from upstream convective sections.

Montana Subbituminous Coal

Utilities firing this Montana high sodium coal at standard or baseline conditions (Figure 13) experience thin molten deposits on waterwall tube surfaces. These deposits are generally controllable by frequent (3 to 6 hours) sootblowing. Severe fouling problems are encountered, particularly in the finishing superheater and finishing reheater surfaces. Thick (3"-12", 8-30 cm) highly sintered strongly bonded deposits develop which cannot be effectively removed with conventional sootblowers. Although the deposit buildup rate is low, frequent blowing is a consequence of the ineffectiveness of sootblowers.

Furnace limestone injection (Ca/S $>$1.0) in a utility firing this coal with a low NO_x firing system (Figure 14) will greatly reduce convective pass deposit to tube bonding strengths to levels controllable with conventional sootblowers overcoming a major problem. Deposit friability and accumulation rate will increase as limestone injection rate is increased. Limestone injection rate may be limited by the insulating effect of lower furnace deposits. FPTF results indicate that limestone addition at Ca/S ratios $>$2.0 will significantly reduce heat transfer through the waterwalls. Therefore, during utility operation, the ability to maintain heat transfer rates in the lower furnace may set the maximum limestone feed rate.

CONCLUSIONS

The application of furnace limestone injection will be fuel and unit specific. Two coals representing a wide range of fouling characteristics were tested at pilot scale: a high iron, high sulfur Midwest bituminous coal and a high sodium, low sulfur Western subbituminous coal. Results indicate that limestone can be injected without adversely affecting the furnace slagging and convective pass fouling performance of units firing these two coals under standard firing conditions. For high sodium coals limestone has significant potential for reducing fouling by weakening deposit to tube bond thereby enhancing sootblower cleaning effectiveness.

Staged combustion resulted in significantly increased slagging for the high iron Midwest coal. Careful thought should be given to the design of commercial low NO_x firing systems for high iron coals to avoid this problem.

With each coal upper limits for limestone addition were established based upon deposit accumulation and/or heat transfer rates. Limits were Ca/S between 2 and 4 for the low sulfur coal and less than 2 for the high sulfur coal. While limestone did not adversely affect the high iron coal investigated, other high iron coals should be examined on an individual basis to avoid potential fluxing effects of calcium on the iron which can increase slagging.

Finally, a laboratory procedure to measure the slagging and fouling consequences of furnace limestone injection was demonstrated. Due to the variability in particular coal properties, utility companies considering this technology would be advised to consider laboratory tests to screen particular coals for their slagging and fouling characteristics.

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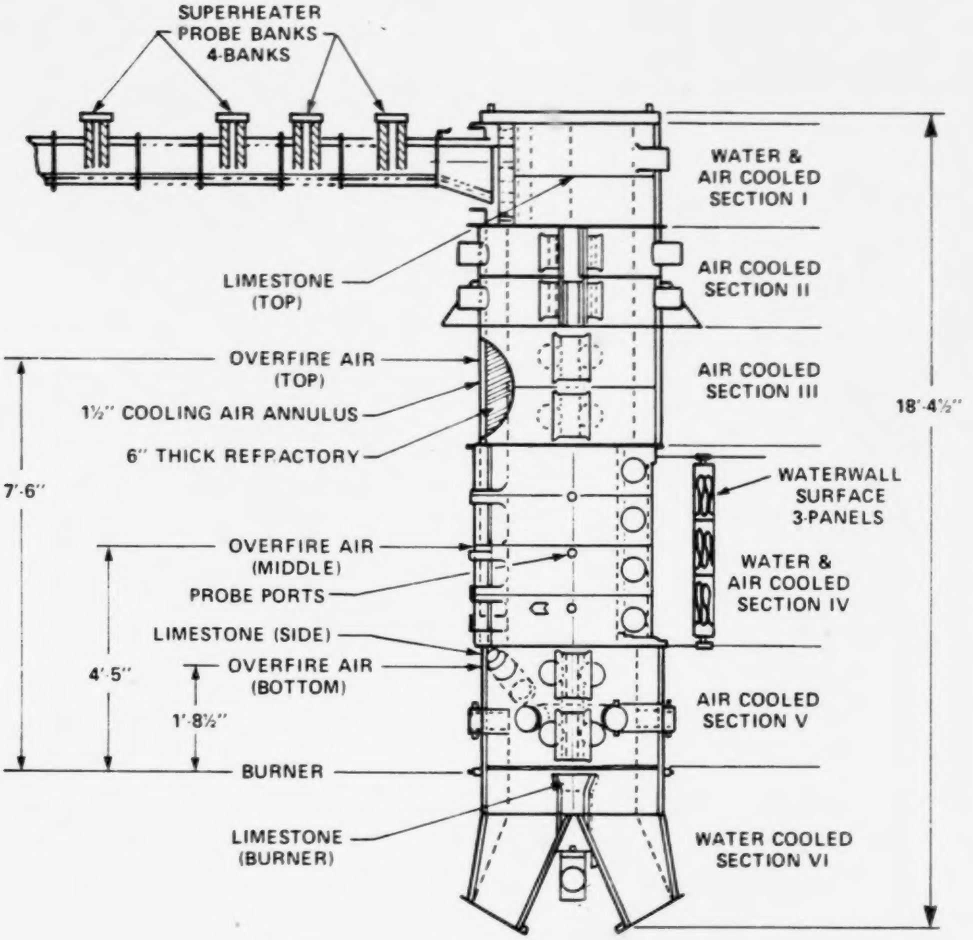

SUPERHEATER PROBE BANKS 4-BANKS
WATER & AIR COOLED SECTION I
AIR COOLED SECTION II
AIR COOLED SECTION III
WATERWALL SURFACE 3-PANELS
WATER & AIR COOLED SECTION IV
AIR COOLED SECTION V
WATER COOLED SECTION VI
18'-4½"
LIMESTONE (TOP)
OVERFIRE AIR (TOP)
1½" COOLING AIR ANNULUS
6" THICK REFRACTORY
7'-6"
OVERFIRE AIR (MIDDLE)
PROBE PORTS
LIMESTONE (SIDE)
4'-5"
OVERFIRE AIR (BOTTOM)
1'-8½"
BURNER
LIMESTONE (BURNER)

Fig. 1: Fireside Performance Test Furnace

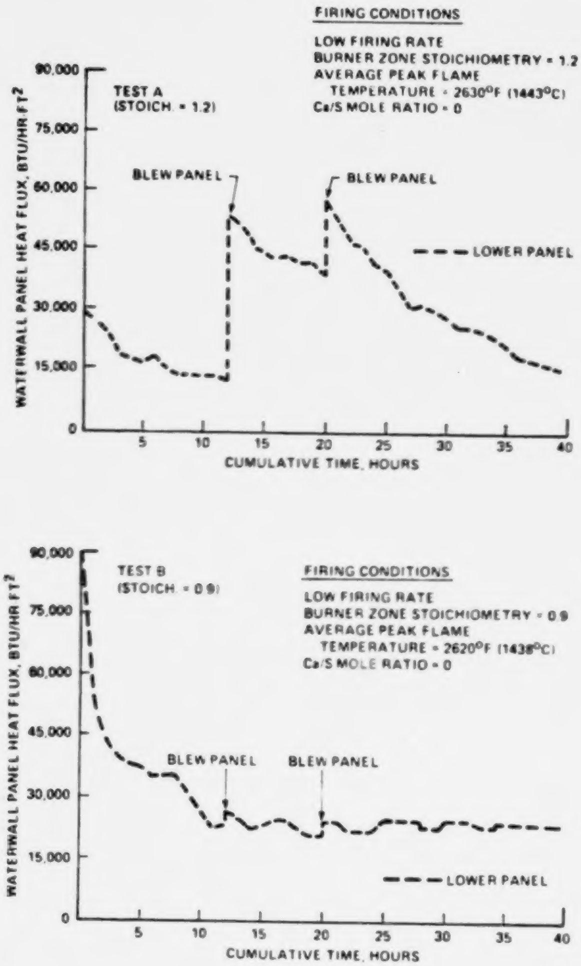


Fig. 2: Illinois #6 Coal Waterwall Panel Heat Flux Curves For Standard and Low NO_x Firing

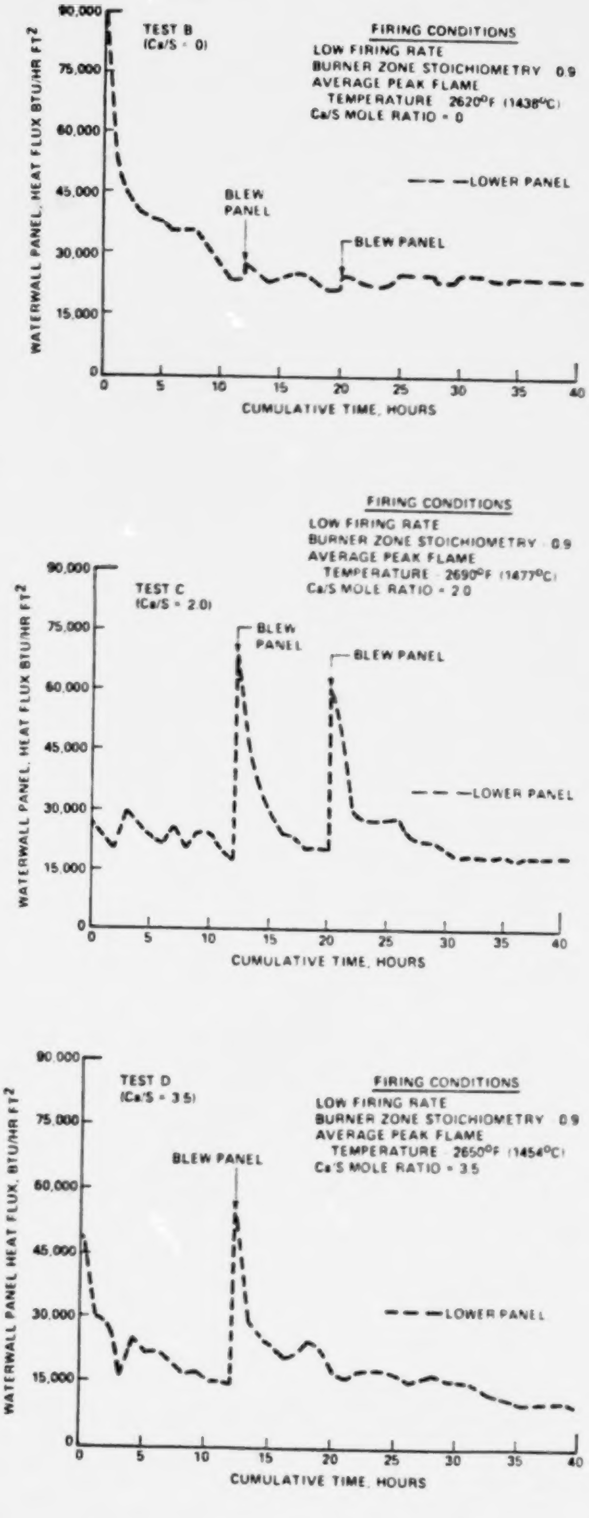


Fig. 3: Illinois #6 Coal Tests B, C and D Waterwall Panel Heat Flux Curves

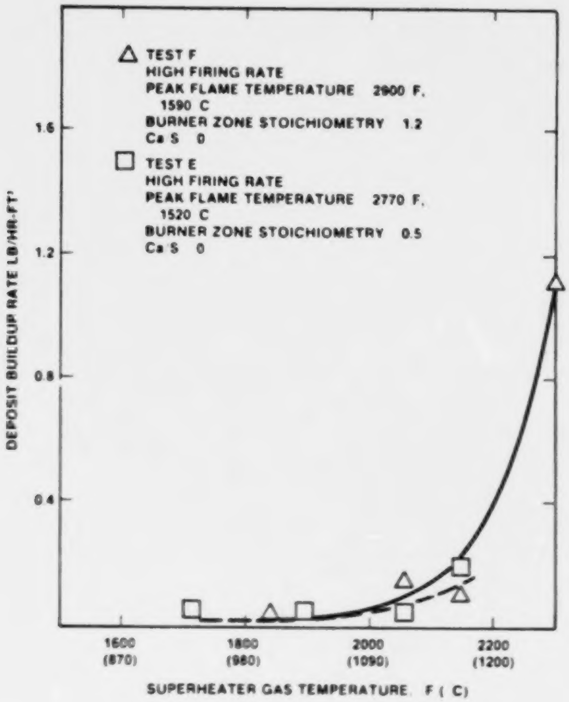


Fig. 4: Illinois =6 Coal Test F and Test E Superheater Probe Deposit Buildup Rate Curves

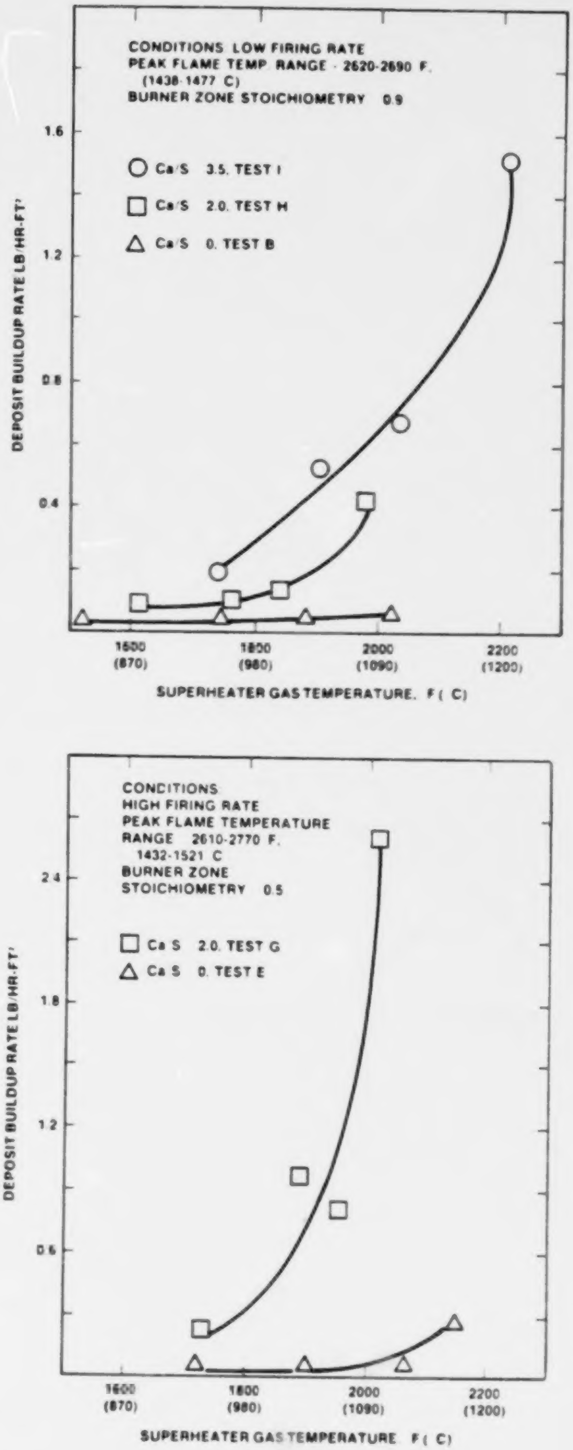


Fig. 6: SO_2 Removal % vs Residence Time in the Temperature Range 2300-1800°F, (1260-980°C) During Illinois =6 Coal Testing

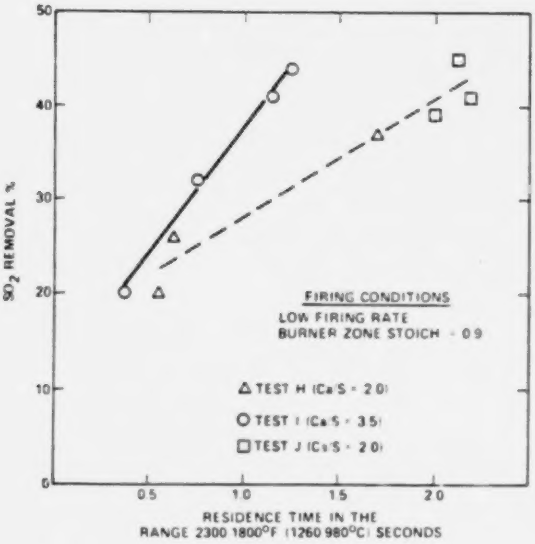


Fig. 5: Effect of Limestone Feed Rate (Ca/S Ratio) on Superheater Probe Deposit Builtup Rate During Low NO_x Firing of Illinois =6 Coal (Two Firing Rates)

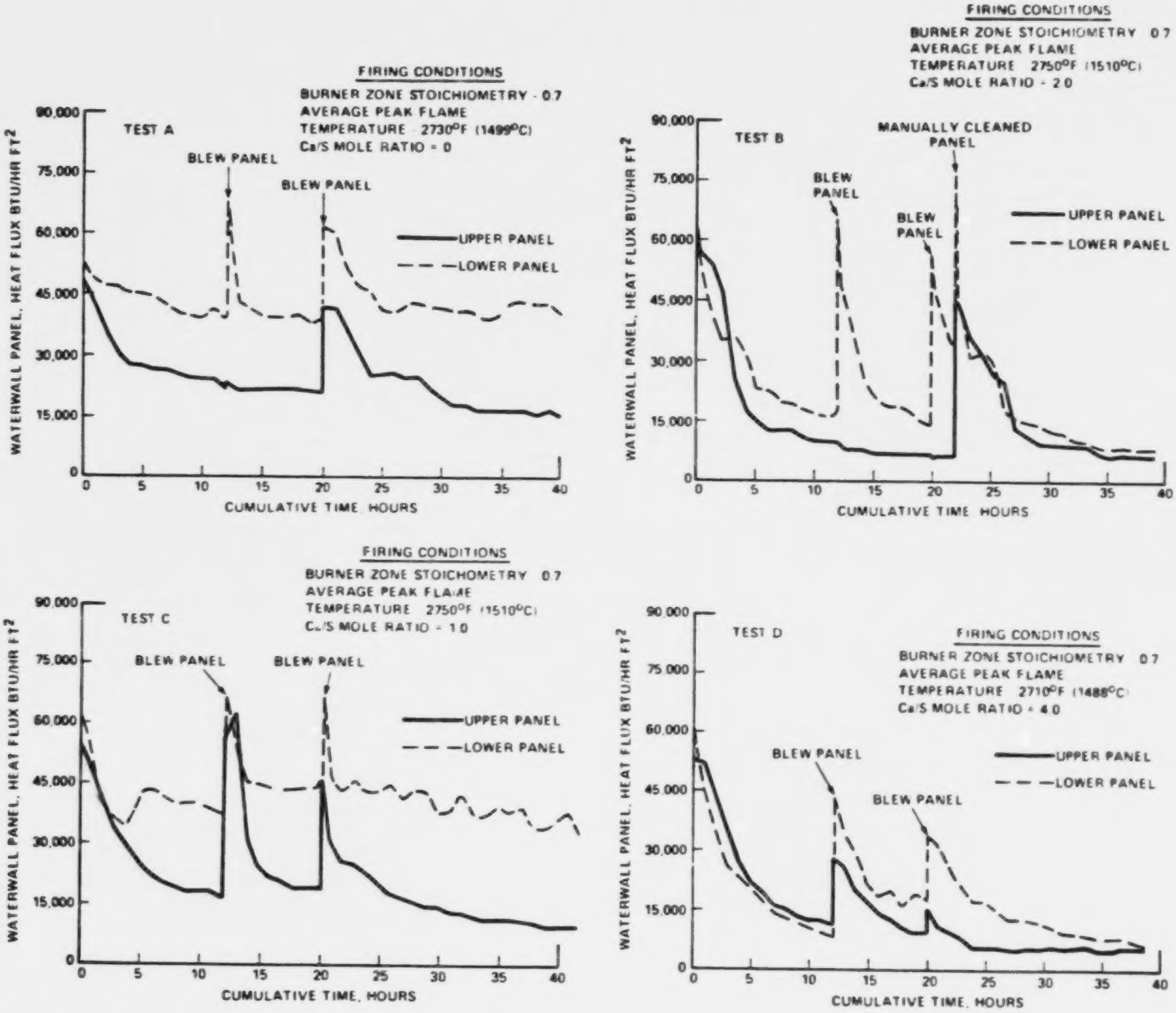


Fig. 7: Montana Subbituminous Coal Waterwall Panel Heat Flux Curves

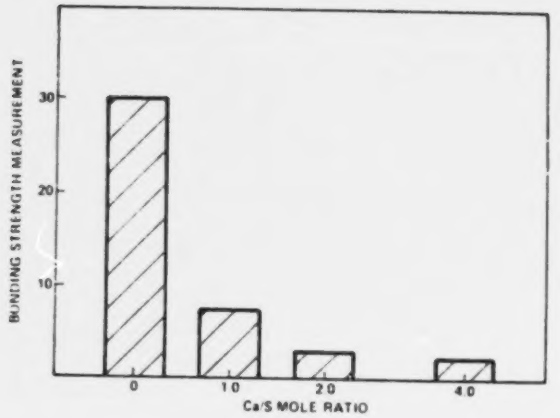


Fig. 8: Montana High Sodium Coal Deposit-to-Tube Bonding Strength as a Function of Ca/S Mole Ratio

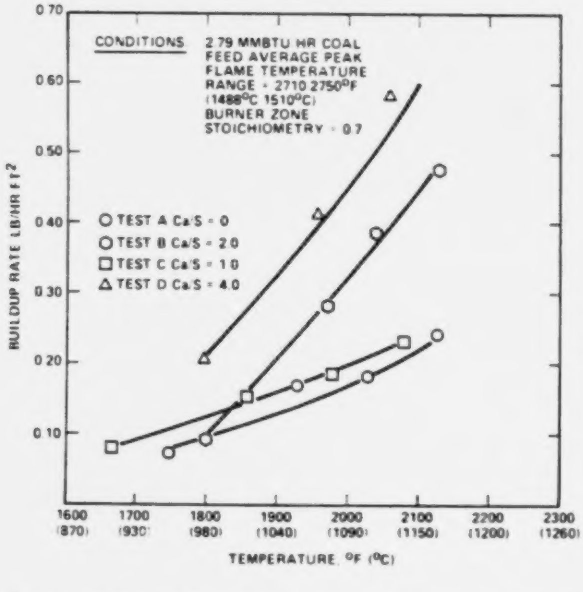


Fig. 9: Effect of Ca/S Ratio on Superheater Probe Deposit Buildup Rate During Montana Subbituminous Coal Testing

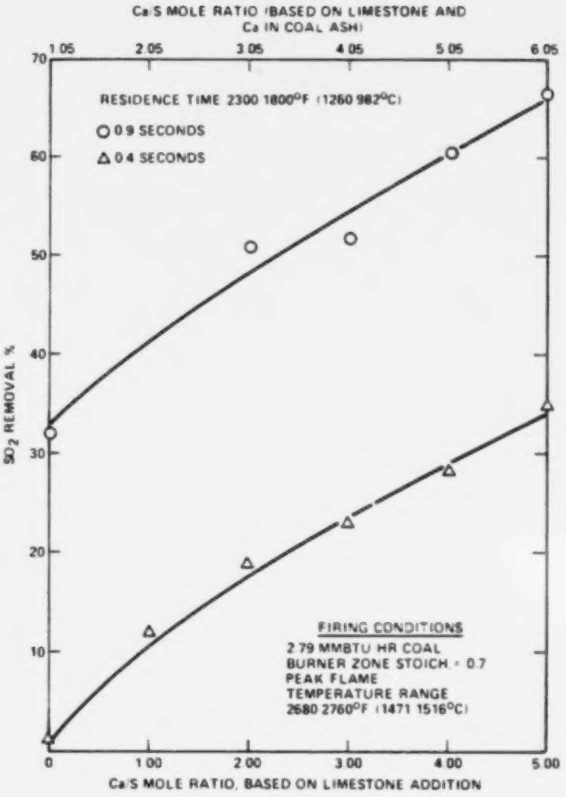


Fig. 10: Effect of Ca/S Mole Ratio on SO_2 Removal at Two Residence Time in the Temperature Range 2300-1800°F While Test Firing A Montana Subbituminous Coal

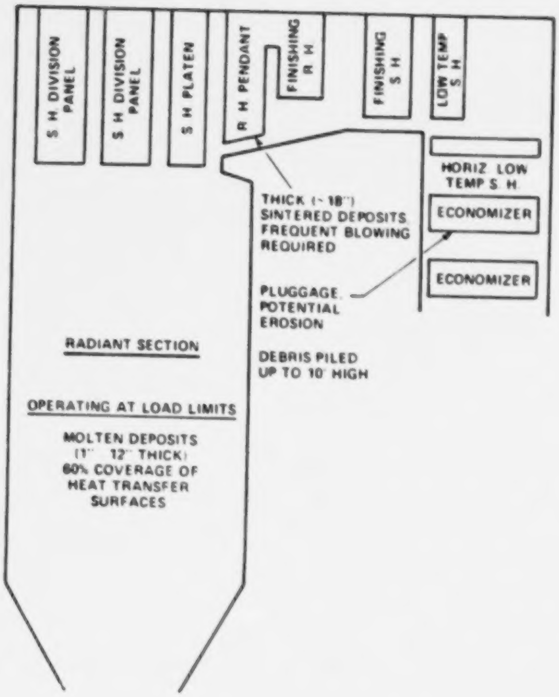
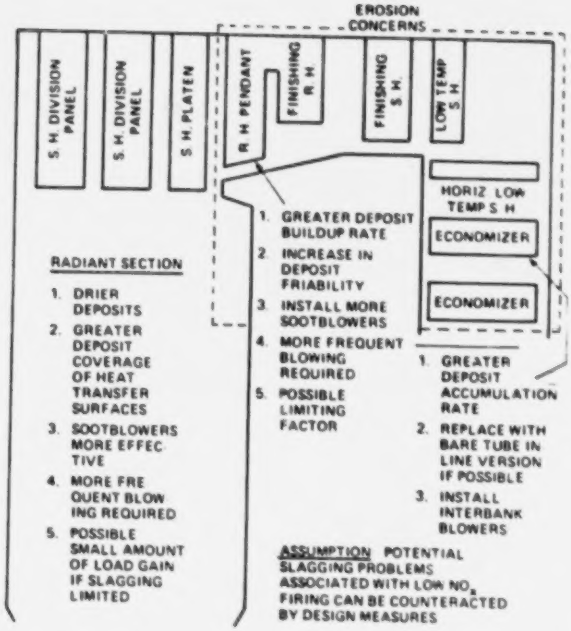

S H DIVISION PANEL
S H DIVISION PANEL
S H PLATEN
R H PENDANT
FINISHING R H
FINISHING S H
LOW TEMP S H
HORIZ LOW TEMP S H
ECONOMIZER
ECONOMIZER
THICK (~ 18") SINTERED DEPOSITS FREQUENT BLOWING REQUIRED
PLUGGAGE POTENTIAL EROSION
DEBRIS PILED UP TO 10' HIGH
RADIANT SECTION
OPERATING AT LOAD LIMITS
MOLTEN DEPOSITS (1" 12" THICK) 60% COVERAGE OF HEAT TRANSFER SURFACES

Fig. 11: Typical Utility Firing Illinois =6 Coal Baseline


EROSION CONCERNS
S H DIVISION PANEL
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FINISHING S H
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ECONOMIZER
ECONOMIZER
RADIANT SECTION
1. DRIER DEPOSITS
2. GREATER DEPOSIT COVERAGE OF HEAT TRANSFER SURFACES
3. SOOTBLOWERS MORE EFFEC TIVE
4. MORE FRE QUENT BLOW ING REQUIRED
5. POSSIBLE SMALL AMOUNT OF LOAD GAIN IF SLAGGING LIMITED
1. GREATER DEPOSIT BUILDUP RATE
2. INCREASE IN DEPOSIT FRIABILITY
3. INSTALL MORE SOOTBLOWERS
4. MORE FREQUENT BLOWING REQUIRED
5. POSSIBLE LIMITING FACTOR
1. GREATER DEPOSIT ACCUMULATION RATE
2. REPLACE WITH BARE TUBE IN LINE VERSION IF POSSIBLE
3. INSTALL INTERBANK BLOWERS
ASSUMPTION POTENTIAL SLAGGING PROBLEMS ASSOCIATED WITH LOW NO$_x$ FIRING CAN BE COUNTERACTED BY DESIGN MEASURES

Fig. 12: Utility Firing Illinois =6 Coal with Limestone Addition (Ca/S = 2.0), Under Low NO_x Conditions at Reduced Flame Temperature (200°F Reduction)

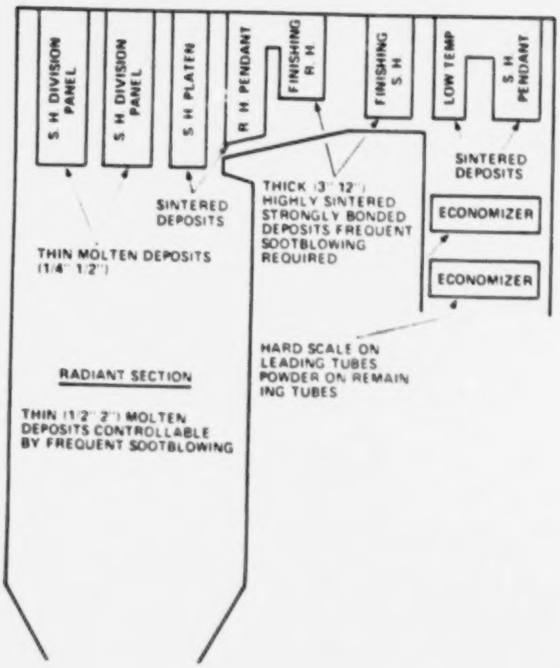
S H DIVISION PANEL
S H DIVISION PANEL
S H PLATEN
R H PENDANT
FINISHING R H
FINISHING S H
LOW TEMP
S H PENDANT
SINTERED DEPOSITS
SINTERED DEPOSITS
THIN MOLTEN DEPOSITS (1/4" 1/2")
THICK (3" 12") HIGHLY SINTERED STRONGLY BONDED DEPOSITS FREQUENT SOOTBLOWING REQUIRED
ECONOMIZER
ECONOMIZER
HARD SCALE ON LEADING TUBES POWDER ON REMAINING TUBES
RADIANT SECTION
THIN (1/2" 2") MOLTEN DEPOSITS CONTROLLABLE BY FREQUENT SOOTBLOWING

Fig. 13: Typical Utility Firing Montana Subbituminous Coal Baseline

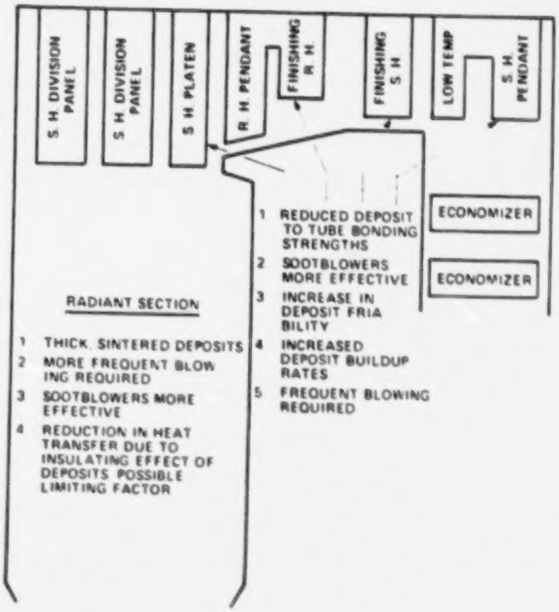
S H DIVISION PANEL
S H DIVISION PANEL
S H PLATEN
R H PENDANT
FINISHING R H
FINISHING S H
LOW TEMP
S H PENDANT
ECONOMIZER
ECONOMIZER
1 REDUCED DEPOSIT TO TUBE BONDING STRENGTHS
2 SOOTBLOWERS MORE EFFECTIVE
3 INCREASE IN DEPOSIT FRIABILITY
4 INCREASED DEPOSIT BUILDUP RATES
5 FREQUENT BLOWING REQUIRED
RADIANT SECTION
1 THICK SINTERED DEPOSITS
2 MORE FREQUENT BLOWING REQUIRED
3 SOOTBLOWERS MORE EFFECTIVE
4 REDUCTION IN HEAT TRANSFER DUE TO INSULATING EFFECT OF DEPOSITS POSSIBLE LIMITING FACTOR

Fig. 14: Typical Utility Firing Montana Subbituminous Coal with Limestone Addition (Ca/S = 2.0) Under Low NO_x Conditions at Reduced Flame Temperature (200°F Reduction)

TABLE 1

COAL, LIMESTONE ANALYSES (AS FIRED)

	Illinois #6 Coal	Montana Coal
Proximate, Weight %		
Moisture	3.2	9.7
Volatile Matter	40.2	40.2
Fixed Carbon	45.4	45.2
Ash	11.2	4.9
Total	100.0	100.0
HHV, Btu/lb	12,070	11,150
(Kcal/Kg)	6,706	6,194
Ultimate, Weight %		
Moisture	3.2	9.7
Hydrogen	4.8	4.9
Carbon	66.5	64.8
Sulfur	3.4	0.5
Nitrogen	1.2	1.0
Oxygen (dif.)	9.7	14.2
Ash	11.2	4.9
Total	100.0	100.0
Ca/S Mole Ratio	0.09	1.05
Alkali/S Mode Ratio[(1)]	0.13	1.96
Ash Composition, Weight %		
SiO_2	52.2	28.4
Al_2O_3	18.6	16.6
Fe_2O_3	14.0	7.8
CaO	3.9	15.5
MgO	0.8	2.5
Na_2O	0.6	6.9
K_2O	1.4	0.2
TiO_2	1.0	1.2
SO_3	4.6	19.5
Total	97.1	98.6
Ash Fusibility, °F (°C)		
I.T.	2130 (1166)	2010 (1099)
S.T.	2200 (1204)	2070 (1132)
H.T.	2380 (1304)	2150 (1177)
F.T.	2420 (1327)	2170 (1188)
Limestone Weight %		
$CaCO_3$		96.7
$MgCO_3$		0.4

Note: 1. Alkali = Ca, Mg, Na, K

TABLE 2

EFFECT OF CONVECTION PASS DEPOSIT THICKNESS ON SO_2 REMOVAL

Ca/S Ratio	Residence Time Between 1800-2300° F (982-1260° C) Sec	Deposit Thickness Inches (CM)	Flue Gas SO_2 PPM	SO_2 Removal %
0	0.6	1 (2.5)	434	5
0	0.6	2 (5.1)	396	13
1	0.8	0.25 (0.6)	341	25
1	0.8	2.25 (5.7)	274	40
2	0.7	1.25 (3.2)	316	31
2	0.8	3.5 (8.9)	191	58
4	0.8	0.75 (1.9)	306	33
4	0.7	2.0 (5.1)	222	51

EFFECTS OF FURNACE SORBENT INJECTION ON FLY ASH CHARACTERISTICS AND ELECTROSTATIC PRECIPITATOR PERFORMANCE

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ABSTRACT

The effects of furnace sorbent injection on the electrical resistivity and the size distribution of particles suspended in flue gas have been studied at temperatures near 149°C (300°F). In situ resistivity and impactor data have been obtained using various sorbents and sorbent injection modes while firing coal in a 1.06 GJ/hr (1×10^6 Btu/hr) combustion system. Laboratory resistivity measurements have also been made with fly ash/sorbent mixtures using various simulated flue gas conditions.

When using a 2.3% sulfur Indiana coal, the fly ash resistivity was in the range of 8×10^8 to 1×10^9 ohm cm at a flue gas temperature of 147 to 153°C (297 to 308°F) and in the presence of 26 to 31 ppm of SO_3 produced from the coal. With burner injection of Vicron 45-3 limestone at a calcium-to-sulfur ratio of 1.8, the resistivity was increased to 1 to 2×10^{12} ohm cm with virtually no measurable SO_3 left in the gas phase at 150 to 158°C (302 to 317°F). Experiments with flue gas conditioning showed that the resistivity of ash/sorbent mixtures produced from limestone injection could be reduced to less than 5×10^{10} ohm cm with the injection of 30 to 40 ppm of SO_3, provided there was adequate residence time for uptake of SO_3. Preliminary data suggest that the effectiveness of SO_3 conditioning may be influenced by sorbent injection temperature when hydrated lime is injected downstream from the burner.

The implications of these and other results on electrostatic precipitator performance are discussed, together with potential corrective measures for improving the collection efficiency of ash/sorbent mixtures.

EFFECTS OF FURNACE SORBENT INJECTION ON FLY ASH CHARACTERISTICS AND ELECTROSTATIC PRECIPITATOR PERFORMANCE

INTRODUCTION

Program Needs

Considerable effort has been directed toward the optimization of sulfur capture in the LIMB (Limestone Injection Multistage Burners) process. This effort has included laboratory studies of the calcination and sulfation processes (1-3) as well as pilot-scale testing of various sorbents (4,5). The work that has been done to date has been successful in identifying sorbents and sorbent injection conditions that are capable of meeting the program goals of 50 to 60% SO_2 removal at a Ca/S ratio of 2:1. At this stage of development, however, neither the sorbent nor the process conditions can be said to be "optimized." There are also a number of unresolved questions concerning the economic constraints on the LIMB process; the effect of the process on boiler slagging, fouling, and reliability; and the effect of the process on particulate control equipment. The last item is the subject of the ongoing study described here.

In a retrofit application, the LIMB process will produce a significant increase in the amount of particulate material that must be handled by the particulate collector. In most cases, the particulate collector will be an electrostatic precipitator (ESP) since ESPs currently service about 92% of the coal-fired electric generating capacity (6). The LIMB process may also alter the particle size distribution and the electrical resistivity of the particulate matter. These are two parameters that can play a critical role in precipitator performance. In addition to these key factors, a retrofit application of LIMB may also affect the operation of the ESP rapper system and the ash handling system. All of these effects must be studied and quantified in order to assess the effect of LIMB on ESP operation. Studies of these effects are also necessary to serve as a basis for making intelligent recommendations concerning potential corrective measures.

Description of LIMB Particulate Research Program

The Environmental Protection Agency's LIMB particulate research program consists of laboratory, pilot-scale, and full-scale measurement programs. Laboratory and pilot-scale work has been underway at Southern Research Institute (SRI) since July of 1982. To date, this work has concentrated on the effect of sorbent injection on the particle size distribution and electrical resistivity of fly ash from pulverized coal combustion. These effects have been studied using various sorbents and sorbent injection modes while firing coal in a 1.06 GJ/hr (1×10^6 Btu/hr) combustor.

Cascade impactors, an optical counter, and an electrical aerosol size analyzer have been used to make in situ measurements of the particle size distribution with and without sorbent injection. The effect of the sorbent injection on the electrical resistivity has been determined from in situ measurements using a point-plane probe in the combustor flue gas at temperatures near 149°C (300°F). Laboratory resistivity measurements have also been made using fly ash and ash/sorbent mixtures collected in the point-plane probe and equilibrated with simulated flue gas environments in the laboratory.

The laboratory and pilot-scale work mentioned above is the subject of this paper. Larger scale work is planned, but will not be described here except to mention the major remaining elements of the LIMB particulate research program. A larger scale, ~85 m^3/min (~3000 ft^3/min), pilot precipitator test program is planned for 1985 using a modified version of EPA's mobile precipitator. Full-scale testing is also planned for 1985 at the Weiher Station in West Germany as a part of the American-German LIMB Technology Transfer Program. Utility-sponsored full-scale measurements with limestone injection using cleaned coal as fuel may be conducted in late 1985 at the Pennsylvania Electric Company's Homer City Station. Precipitator performance and particulate characterization measurements are also planned for EPA's LIMB Demonstration Program at a full-scale power station during 1987.

Objectives and Scope of This Study

The goal of this study was to develop information that could be used to assess the probable effects of a LIMB retrofit on ESP performance, and suggest potential corrective measures to restore acceptable ESP performance. An assessment of this type requires data on the effect of sorbent injection on: the particle size distribution, the electrical resistivity, the ESP rapping requirements and reentrainment, and the operation of the ash handling system. To date, the scope of this study has been limited to the first two factors: particle size distribution and resistivity. Larger scale studies will provide the information concerning the effects on the rapping and ash handling systems.

One of the first major objectives of this study was to verify that the pilot combustor produced a fly ash that was an acceptable representation of that produced when the same coal was burned in a full-scale boiler. The characteristics of the fly ash produced in the pilot combustor were compared to the characteristics of fly ash from a full-scale (196 MW) boiler that was firing the same coal. This involved comparisons of the ash particle size distributions, electrical resistivities, morphologies, and chemical compositions. These comparisons, which are described in detail elsewhere (7), revealed excellent correspondence between the fly ashes from the pilot-scale combustor and the full-scale boiler. Thus, it was concluded that the ash simulation capabilities of the combustor were adequate for the follow-on studies with sorbent injection.

TESTING PROCEDURES AND EQUIPMENT

Pilot-Scale Combustion Research Facility

Figure 1 presents a schematic diagram of the SRI pilot-scale combustion research facility. The system includes a refractory-lined furnace which can fire either coal or natural gas at a rate of 0.63 to 1.27 GJ/hr (0.6 to 1.2 x 10^6 Btu/hr). The furnace is followed by both air- and water-cooled heat exchangers, and by a pulse jet baghouse. A forced draft and an induced draft fan are used so that the system can be operated as a balanced draft unit. System design temperatures and gas velocities for the principal sections are given in Table 1.

The down-fired furnace is equipped with a modified version of EPA's Distributed Mixing Burner with outboard, tertiary air ports for staging. Sorbent injection points are located at the burner core and at seven locations between the burner and the outlet of the horizontal duct (see Figure 1). Both the coal and the sorbent are metered with Acrison gravimetric feeders. The sorbent may be aspirated into the primary air line for burner injection, or into a separate transport airstream for injection at other locations.

As shown in Figure 1, an isothermal residence chamber has been installed in the back-end of the system where the gas temperature is typically about 149°C (300°F). This chamber provides a gas residence time of about 1 sec in which the conditions are nearly isothermal. This simulates the time-temperature interval between the air heater and the ESP in a power plant. The simulation of this part of the ash thermal history is critical to the uptake of SO_3 and its effect on resistivity. The sampling port for the particle size and resistivity measurements is located just downstream from the isothermal residence chamber. The effect of SO_3 conditioning may be studied using a conditioning system that has been installed upstream of the isothermal residence chamber. This system consists of an electrically heated catalytic reactor and injection line. Sulfur dioxide is metered from a gas cylinder and passes through the catalytic reactor where it is converted to SO_3. The resulting SO_3 is then injected into the flue gas at a point upstream of the residence chamber to allow adequate mixing and sufficient time for uptake on the particulate.

Sampling Equipment and Procedures

Particle Size Distribution Measurements. Particle size distribution measurements were made using a combination of Modified Brink Model BMS-11 Cascade Impactors, a Thermo-Systems Model 3030 Electrical Aerosol Size Analyzer, and a Climet Model Cl-208C Optical Particle Counter. The general procedure for the use of cascade impactors has been described by Harris (8). The Brink impactors used in this study were equipped with a precutter cyclone, six impactor stages, and a backup filter. Lightweight glass fiber substrates were used on the impaction stages. The impactor was inserted into the flue gas stream and allowed to reach gas temperature before beginning the impactor sampling. The sampling rate was adjusted to sample isokinetically with the centerline velocity at the resistivity port. Each set of impactor measurements (with and without sorbent) consisted of 12 impactor runs, 2 of which were blank runs. The blank runs were performed with a filter ahead of the impactor, so that any substrate weight changes caused by flue gas-substrate interaction could be quantified and taken into account. The blank corrections were generally quite small compared to the particulate mass collected on the impaction stages. The raw impactor data were reduced using the Cascade Impactor Data Reduction System (CIDRS) developed by Johnson et al. (9,10). This yields size distribution data for particles in the range of 0.5 to 10 μm.

For finer particles in the range of 0.01 to 0.5 μm, it was necessary to use an electrical aerosol size analyzer (EASA) in combination with an optical particle counter (OPC). The operating principles of these instruments have been reviewed by Liu and Pui (11) and Liu et al. (12). These instruments are designed to handle relatively low particulate concentrations at room temperature. Therefore, the sample to be analyzed must be extracted from the flue gas, cooled, and diluted prior to examination in the EASA or OPC. The sample extraction and dilution system that was used in this study has been described by Felix et al. (13). Extensive testing has been done to verify that secondary aerosols are not produced in the sample extraction and dilution system. The EASA and OPC data were obtained concurrently with the impactor data. All three data sets were combined to form a complete size distribution over the range of 0.01 to 10 μm, with and without sorbent injection.

In Situ Resistivity and SO_3 Measurements. A modified version of the SRI point-plane resistivity probe was used to obtain in situ resistivity data. The in situ resistivity test methods have been described by Nichols and Banks (14). The resistivity was calculated from the voltage drop across the precipitated dust layer and the electrical current density through the layer immediately prior to electrical breakdown.

Measurements of the gas-phase SO_3 concentrations were made by the modified controlled-condensation technique described by Cheney and Homolya (15). A quartz wool plug was used to remove particulate ahead of the SO_3 condenser. The quartz wool plug was maintained at 274°C (525°F) to prevent uptake of SO_3 on the particulate collected on the plug. This has been found to be satisfactory in sampling ash-laden flue gas from coal-fired boilers (15). However, the loss of SO_3 to the particulate may be a problem in the presence of reactive sorbent. Therefore, the SO_3 data reported here must be regarded as lower limits on the levels actually present in the flue gas.

Laboratory Resistivity Measurements. Samples of fly ash alone and mixtures of fly ash in combination with reacted sorbent were taken from the cavity of the in situ resistivity probe for laboratory analysis. The samples were placed in ASME PTC-28 test cells and heated to 450°C (842°F) in air containing 8% by volume water vapor. The oven was then turned off and the resistivity was determined as a function of descending temperature over the range of 450 to 85°C (842 to 185°F). These measurements were made in accordance with IEEE Standard 548-1981.

For measurements made with SO_3 in the environment, the samples were placed in a radial resistivity test cell designed by Bickelhaupt (16). The cell was placed in an oven and maintained at a constant temperature near 150°C (302°F). Air containing 8% moisture and a known level of SO_3 was passed over the test cell, and the resistivity was monitored until an equilibrium condition was attained. The result obtained by this method represents the minimum resistivity value that can be attained in flue gas containing the prescribed level of SO_3. The in situ resistivity will be higher than the laboratory value if the dynamic interaction of the particulate and SO_3 in the flue gas does not approach the equilibrium situation.

RESULTS AND DISCUSSION

Effect of Sorbent Injection on SO_2 Capture

The effect of sorbent injection on particulate properties is related to the extent of conversion of the calcined sorbent to a sulfated material. The conversion, or utilization, of the sorbent is a function of a number of process variables including: sorbent type, chemical composition, surface area, particle size, sorbent injection location, injection rate (Ca/S ratio), mixing, and furnace conditions. Since a detailed particulate characterization program cannot be performed with all possible process options, sorbents and injection modes have been chosen for study which have a significant probability of practical application. Most of the data obtained thus far in the particulate program have been with Vicron limestone as the sorbent, although data with a commercial grade of calcium hydroxide, known as Longview hydrated lime, are now being obtained because of the greater effectiveness of this hydrated lime in reacting with SO_2. Characteristics of Vicron and Longview sorbents are given in Table 2.

Figure 2 shows the percentage SO_2 removal obtained in the SRI pilot plant by injection at S-3 at a temperature of approximately 1316°C (2400°F) with Vicron and with two hydrated limes. These data were obtained with a 2.3% sulfur Indiana bituminous coal. The proximate and ultimate analyses of the coal are given in Table 3. The same coal was used for the particulate studies. Although the hydrated limes are more effective than limestone, they are also more expensive on a cost-per-unit-weight basis. Southern Research Institute and the Dravo Lime Company are beginning a project with the objective of developing cost-effective sorbents from limestones. Precalcination, hydration, and the use of promoters to enhance reactivity are approaches which will be evaluated during the course of this project.

Effect of Sorbent Injection on In Situ Resistivity

Since any furnace injection process will produce mixtures of fly ash and partially sulfated calcine, results obtained with Vicron limestone are expected to be at least qualitatively indicative of the effects of LIMB on ash collectability. Therefore, laboratory and in situ resistivity measurements have been made to determine the effects of Vicron injection on resistivity and to evaluate the response of the ash sorbent mixtures to SO_3 conditioning and moisture conditioning.

Figure 3 summarizes the in situ resistivity data obtained with the 2.3% sulfur Indiana bituminous coal with and without burner injection of Vicron limestone at a nominal calcium-to-sulfur ratio of 2:1. Table 4 gives the chemical compositions of the fly ash and the ash/sorbent mixture produced with the Indiana coal with and without Vicron injection. No SO_3 was added to the flue gas. The SO_3 concentration variations shown without Vicron addition were obtained by varying the flue gas cooling regime using the water-cooled heat exchangers ahead of the resistivity probe. The lowest level of SO_3 corresponded to the greatest amount of water cooling. For the measurements made with Vicron addition, the SO_3 level was adjusted by varying the amount of excess air used in the furnace. An SO_3 level of <0.2 ppm corresponded to 2.2% O_2 in the flue gas, and an SO_3 level of 7.9 ppm corresponded to 6.5% O_2 in the flue gas.

Several observations can be made from an examination of Figure 3:

- The in situ data at the lower flue gas temperature without Vicron approach the equilibrium resistivity values predicted by Bickelhaupt (17).
- If no residual SO_3 is present, ash/sorbent mixtures exhibit in situ resistivities of $\sim 10^{12}$ ohm cm.
- Small residual SO_3 concentrations have a dramatic effect on the resistivity of ash/sorbent mixtures. The presence of the sorbent appears to increase the response of the fly ash to a given SO_3 concentration at relatively high flue gas temperatures (~199°C/390°F).
- Resistivity values in the range for good precipitator operation can be achieved for Vicron/ash mixtures in the presence of relatively low residual SO_3 concentrations, when the source of SO_3 is oxidation of naturally occurring SO_2.

Resistivity measurements have also been made with artificially added SO_3 for conditions that result in negligible naturally occurring SO_3. These measurements indicate that resistivity attenuation can be achieved with the injection of 30 to 40 ppm of SO_3, but that the residual levels of SO_3 are sensitive to the residence time in the flue gas and the injection temperature, as well as the concentration of injected SO_3. Additional experiments are planned with varying injection levels, residence times, and measurement temperatures.

In situ measurements with SO_3 injection for conditioning with hydrated lime sorbent have produced ambiguous results. In situ resistivity values of 3 to 7 x 10^{11} ohm cm in the presence of 1.5 to 2 ppm of residual SO_3 have been observed at temperatures of 132 to 143°C (270 to 290°F) when hydrated lime is injected near the furnace exit. Other data indicate that resistivity values of 3 to 7 x 10^{10} ohm cm in the same temperature range are obtained in the presence of 0.5 to 1.2 ppm residual SO_3 when the hydrate is injected nearer the flame zone. Additional work is planned to define the dynamic relationship between resistivity measurement temperature, injection location for the sorbent, injected levels of SO_3, resistivity, and residual SO_3 levels for both limestone and hydrated lime. The preliminary data suggest that hydrated lime injected near the furnace exit may produce a particulate mixture difficult to condition because of the high reactivity of the unsulfated calcine which remains when the mixture reaches the resistivity port.

A small wire-plate precipitator with conventional electrode geometry has been installed in the pilot plant. Voltage-current relationships obtained with this device will be used to augment the resistivity data in evaluating the effectiveness of SO_3 conditioning. Water conditioning at reduced flue gas temperatures, and other potential conditioning agents, will also be evaluated.

Effect of Sorbent Injection on Laboratory Resistivity

Laboratory resistivity measurements were performed for Indiana fly ash from furnace tests with and without Vicron addition. These measurements were conducted with standard procedures developed by Bickelhaupt (16). Water vapor concentrations were varied between 7.9 and 18.7% by volume in air, and the sulfur trioxide concentration was either zero or approximately 5 ppm. For the tests involving sulfur trioxide, the ash layer and the environment were assumed to be in equilibrium when the resistivity value decreased at a rate of less than 30% in a 24-hr period. Figure 4 summarizes results obtained from these experiments. All ash samples were collected in the combustion system resistivity probe. The chemical analyses of the ash samples used in these experiments were given in Table 4. Several observations can be made from these data:

- The presence of the partially sulfated sorbent increased the response of the ash resistivity to a given SO_3 concentration. This confirms the trend shown by the in situ data in Figure 3. Five ppm of SO_3 in the environment decreased the resistivity at 149°C (300°F) by over 3 orders of magnitude.
- The ash/sorbent mixture responds to water conditioning, but it appears that temperatures lower than 93°C (200°F) would be required to lower resistivity into the low 10^{10} ohm cm range with water vapor concentrations of 16 to 19% by volume if no SO_3 is present.
- Resistivities of $\sim 2 \times 10^{12}$ ohm cm are measured for ash sorbent mixtures at hot-side ESP operating temperatures of 300°C (572°F).

Laboratory resistivity measurements have been performed with ash/sorbent mixtures produced with injection of hydrated lime downstream of the burner with the Indiana coal as fuel. Results from these experiments are similar to those shown in Figure 4.

Effect of Sorbent Injection on the Particle Size Distribution

Particle size distribution measurements have been performed with Vicron injected at the burner and downstream from the burner at approximately 1204°C (2200°F). Measurements were also made with hydrated lime injected downstream at the same temperature. The ultrafine system (EASA and OPC) sampled the aerosol from the combustor under conditions which allowed acquisition of the comparative data sets shown in Figures 5 and 6. Figure 5 illustrates that for burner injection the Vicron has no effect on the concentration of ultrafine particles with diameters below 0.1 μm. In the fine particle diameter range of 0.1 to 0.6 μm, however, the mass concentration was increased by a factor of 3 to 4 with burner injection. Figure 6 illustrates that downstream injection eliminates the fine particle concentration increase observed with burner injection, suggesting that the limestone breaks apart under the intense calcination conditions encountered in the flame zone. Injection of hydrated lime at the downstream injection point produced results identical to those observed with downstream injection of Vicron in the ultrafine size range.

PREDICTED EFFECT ON ESP PERFORMANCE

Since downstream injection of limestone generally produces superior SO_2 capture compared to burner injection, without the problem of excessive fine particle production, this mode of sorbent injection was chosen for precipitator performance simulations using the EPA/SRI model (18). The model simulations were performed to evaluate the effects of sorbent addition on ESP performance. The potential effects of ESP design modification and SO_3 conditioning for counteracting the effects of sorbent injection were also investigated.

A particle size distribution was constructed from impactor and ultrafine data with downstream injection of Vicron limestone. The baseline and with-sorbent distributions are presented in Figure 7, on a basis of cumulative mass per unit volume of gas as a function of particle diameter. Electrical data for the simulations were defined from the following assumptions:

- The fly ash resistivity without sorbent was 2×10^{10} ohm cm.
- Vicron addition produced 2×10^{12} ohm cm dust without conditioning.
- SO_3 conditioning restored resistivity of the ash/sorbent mixture to 2×10^{10} ohm cm.

The objective of these simulations was to examine the predicted precipitator performance for existing and modified precipitators in a specific collection area range likely to be encountered in a retrofit application of LIMB technology. Electrode modifications were simulated which consisted of adding a precharging section with conventional electrode geometry, followed by three collecting sections with 0.95-cm (3/8-in.) diameter wires with 22.9-cm (9-in.) plate spacing. These modifications are intended to increase the collection efficiency within the constraints imposed by the existing precipitator installation. The ESP mechanical parameters are provided in Table 5, and the electrical parameters are summarized in Table 6. The parameters assumed for the retrofit electrode modifications are given in Table 7. The particle charge values calculated for the precharger exit are similar to those expected at the exit of a cold-pipe precharger, which has been developed by Denver Research Institute (19).

Figure 8 presents the results of the simulations of collection efficiency for the indicated cases, and Figure 9 provides the ESP performance in terms of nanograms of outlet mass loading per Joule, or pounds of outlet mass loading per 10^6 Btu. These graphs show that, as expected, the high resistivity and increased mass loading associated with LIMB sorbent addition produce unacceptably high emissions. If electrical conditions are restored by SO_3 conditioning, the precipitator collection efficiency is increased over the baseline case (as a result of space charge and the higher concentration of larger particles resulting from sorbent injection), but the outlet emissions are still approximately 45% greater than the baseline case. However, the two-stage retrofit geometry further increases efficiency and results in predicted outlet mass loadings which closely approach the baseline case.

These simulations must be regarded as preliminary, and they will be repeated when experimental electrical data are available with LIMB-generated particulate for the assumed electrode geometry. Additional simulations are planned for hydrate injection when more definitive in situ resistivity data and particle size data are available for this process mode.

CONCLUSIONS

Furnace injection of calcium-containing sorbents produces high resistivity ash/sorbent mixtures in the absence of small residual concentrations of sulfur trioxide. With limestone as the sorbent, resistivity can be reduced to acceptable levels with SO_3 conditioning. If hydrated lime is the sorbent, the in situ response of resistivity to SO_3 is dependent upon the location of sorbent injection in the furnace.

With both limestone and hydrated lime as sorbents, the resistivity of the resulting ash/sorbent mixture is reduced to less than 10^{10} ohm cm at equilibrium with 5 ppm SO_3 and 8% water vapor at 149°C (300°F). The resistivity of ash/sorbent mixtures produced with limestone injection is also reduced by increasing water vapor concentrations. Additional data are required to define the relationship between in situ resistivity, injected SO_3, and residual SO_3 levels.

Burner injection of Vicron limestone produces large increases in submicron particle concentrations in the 0.1- to 0.6-µm diameter range compared with coal firing without sorbent injection. Injection of either Vicron limestone or hydrated lime near the furnace exit did not produce an increase in fine particle concentrations, as determined by an ultrafine sampling system. Downstream injection of Vicron produced a cumulative mass loading at 10-µm diameter approximately 60% greater than the baseline case at a nominal calcium-to-sulfur ratio of 2 to 1.

Simulations of precipitator performance indicate that outlet emissions of less than 43 ng/J (0.1 lb/10^6 Btu) are achievable with sorbent injection at a specific collection area of 59 m^2/m^3/sec (300 ft^2/1000 ft^3/min) if conditioning restores electrical conditions to the values obtained prior to sorbent addition. Modifications of electrode geometry, when combined with a successful conditioning process, have the potential of significantly increasing performance over the values predicted for conventional ESP designs.

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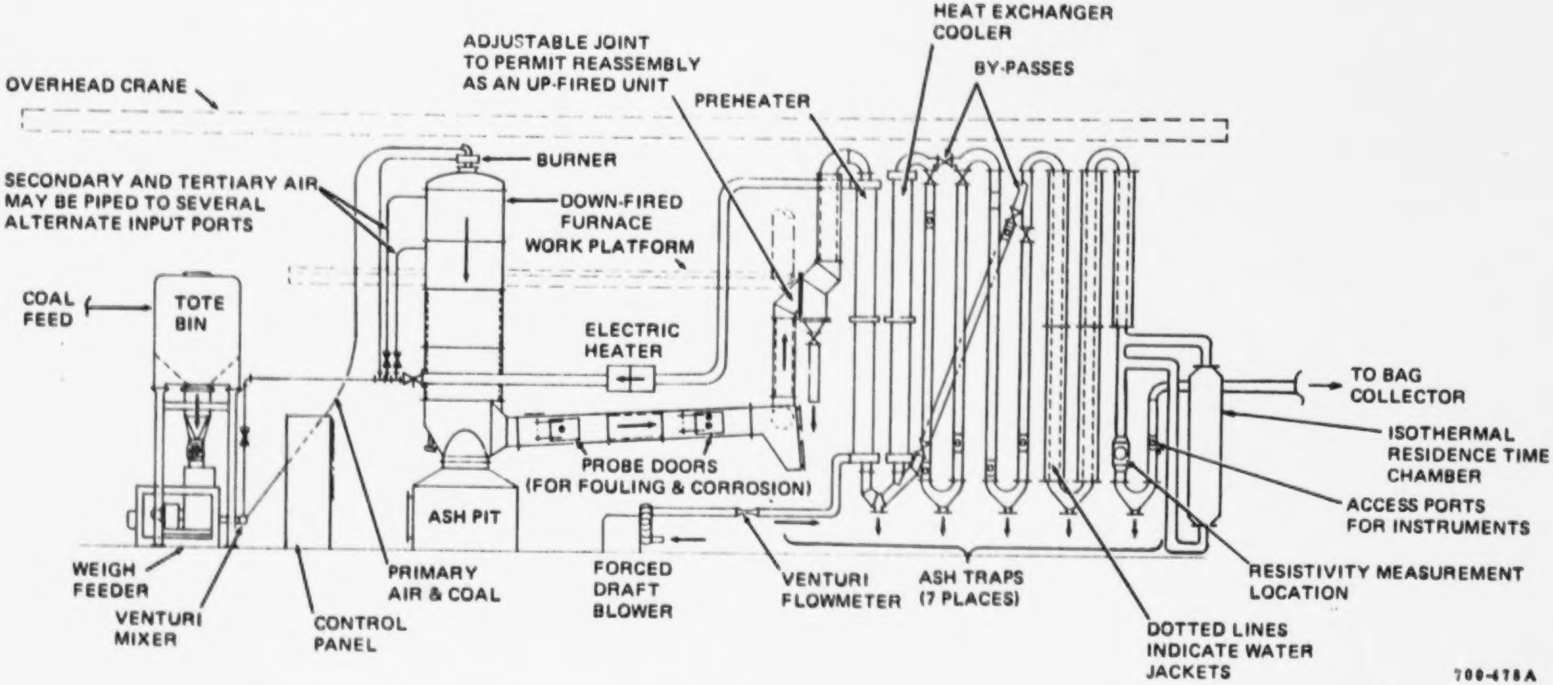
OVERHEAD CRANE
ADJUSTABLE JOINT TO PERMIT REASSEMBLY AS AN UP-FIRED UNIT
PREHEATER
HEAT EXCHANGER COOLER
BY-PASSES
SECONDARY AND TERTIARY AIR MAY BE PIPED TO SEVERAL ALTERNATE INPUT PORTS
BURNER
DOWN-FIRED FURNACE
WORK PLATFORM
COAL FEED
TOTE BIN
ELECTRIC HEATER
TO BAG COLLECTOR
ISOTHERMAL RESIDENCE TIME CHAMBER
PROBE DOORS (FOR FOULING & CORROSION)
ASH PIT
ACCESS PORTS FOR INSTRUMENTS
WEIGH FEEDER
VENTURI MIXER
CONTROL PANEL
PRIMARY AIR & COAL
FORCED DRAFT BLOWER
VENTURI FLOWMETER
ASH TRAPS (7 PLACES)
RESISTIVITY MEASUREMENT LOCATION
DOTTED LINES INDICATE WATER JACKETS
700-478A

Figure 1. Pilot plant used for particulate characterization studies.

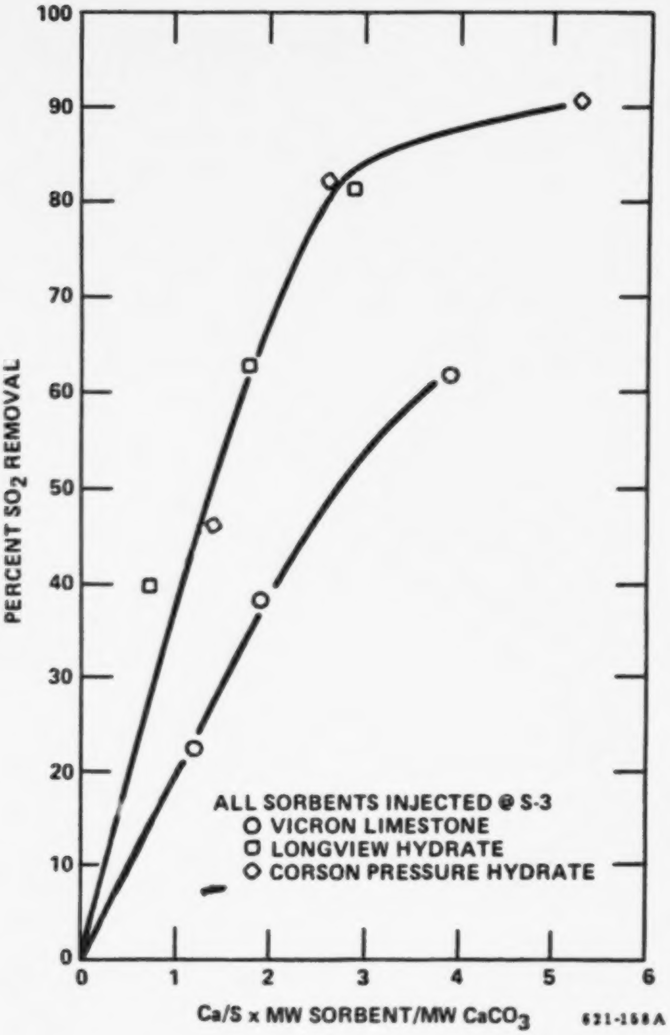

Figure 2. Comparison of various sorbents on a mass basis.

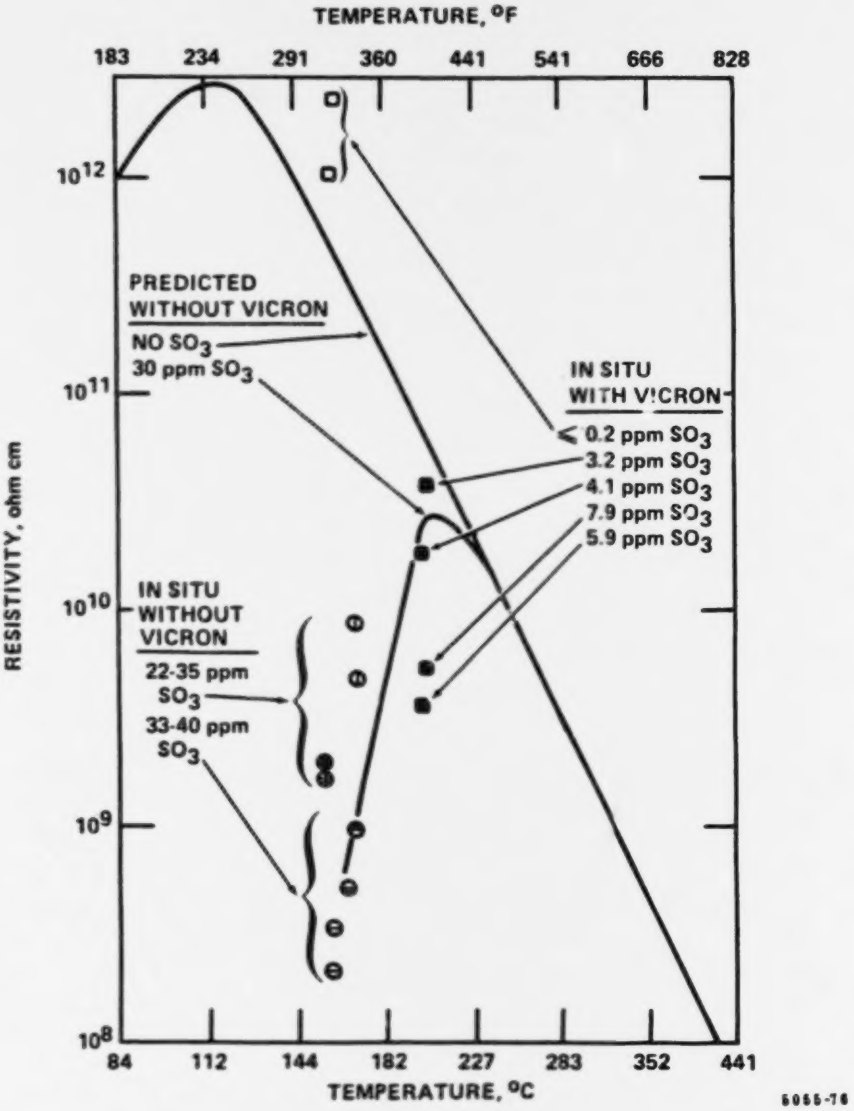

Figure 3. Effect of burner injection of Vicron on the in situ resistivity obtained with 2.3% sulfur Indiana bituminous coal.

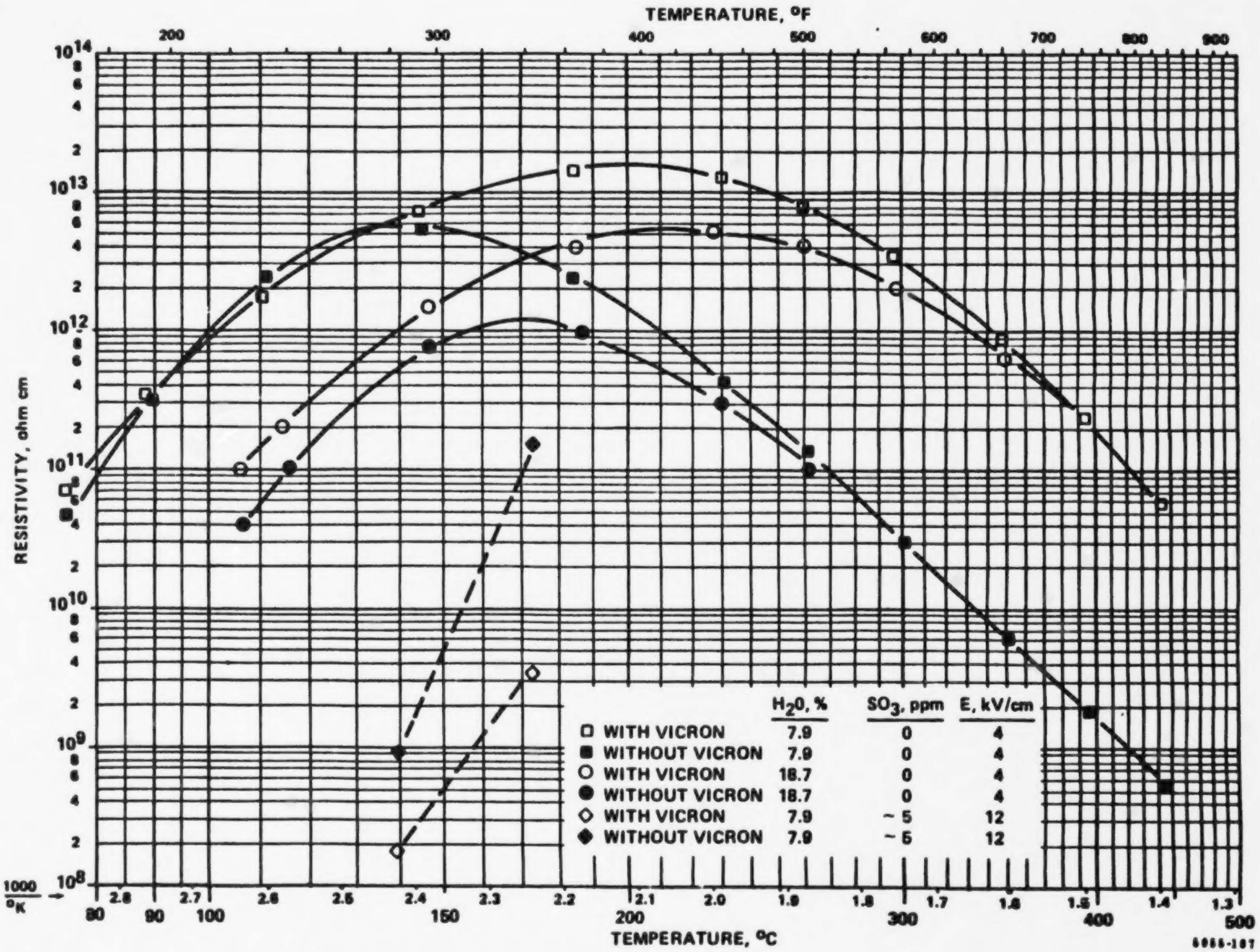

Figure 4. Comparison of resistivities with and without Vicron addition - Indiana 2.3% sulfur bituminous coal.

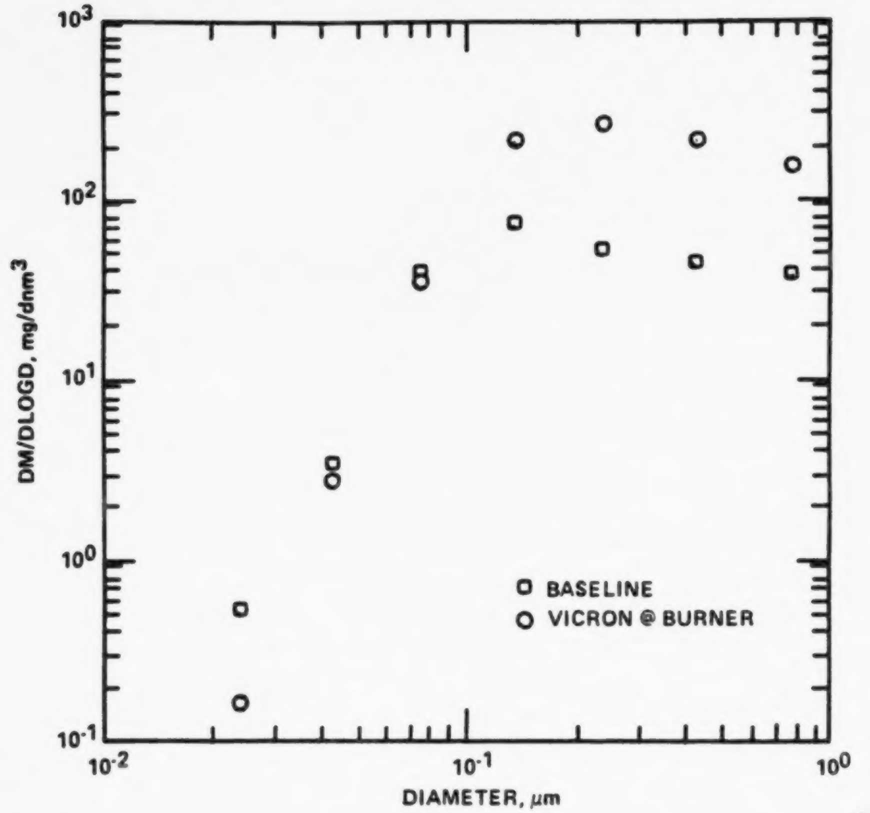

Figure 5. Effect of burner injection of Vicron on the particle size distribution obtained with 2.3 % sulfur bituminous coal.

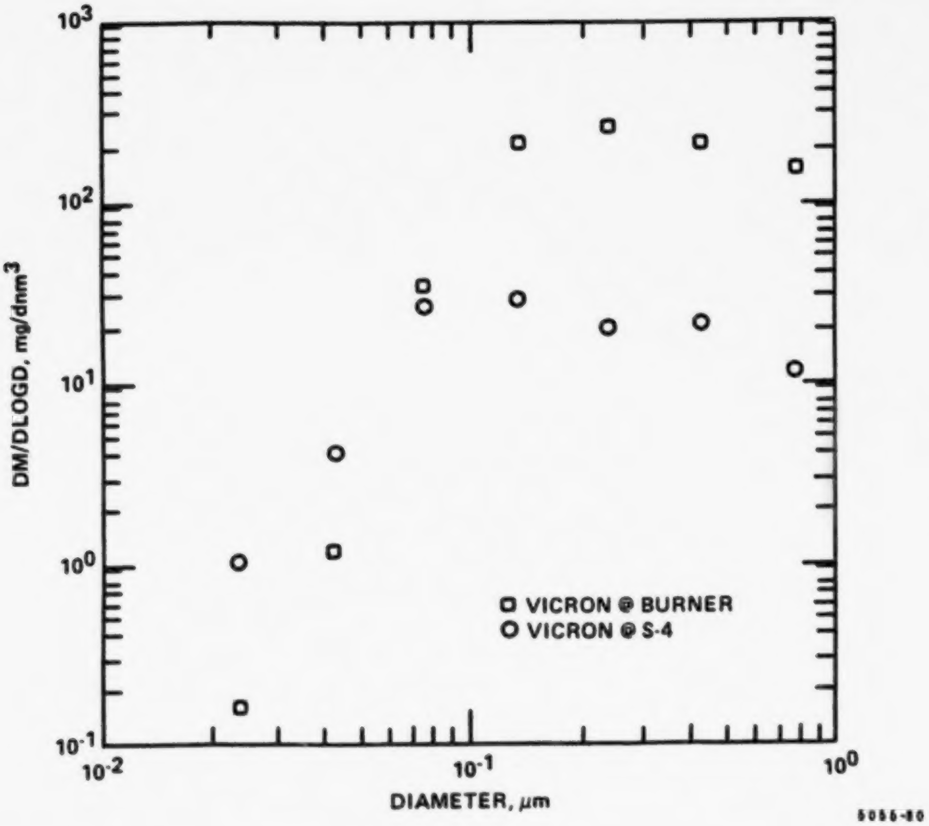

Figure 6. Effect of Vicron injection at S-4 on the particle size distribution compared to the effect of burner injection.

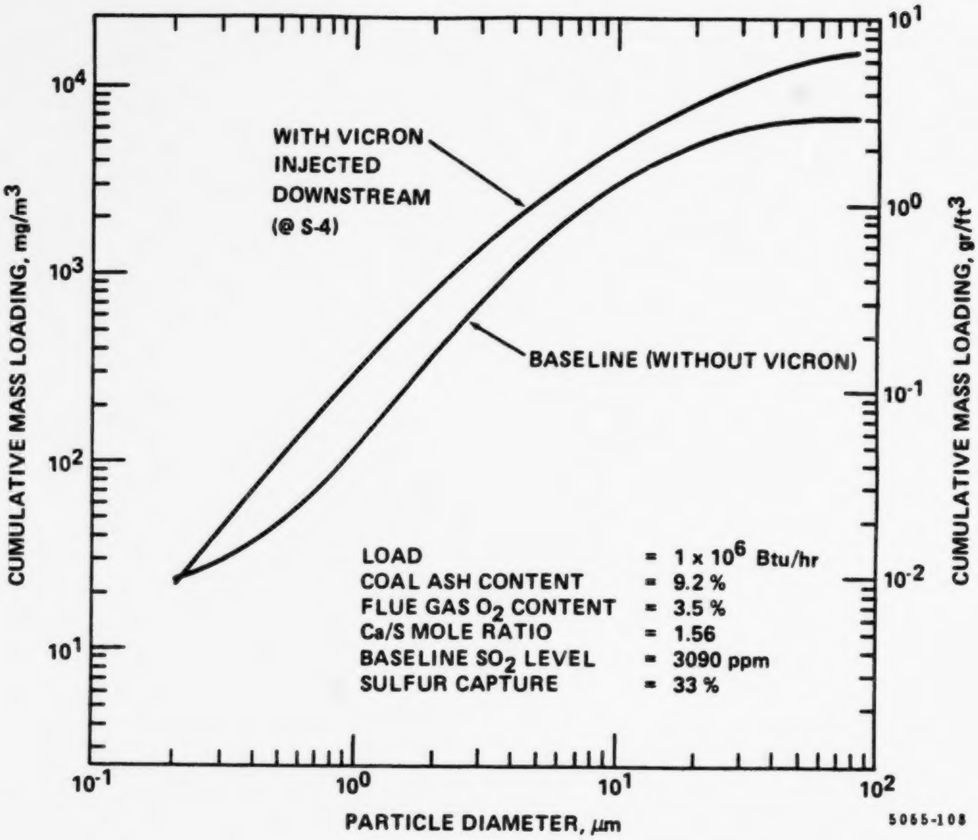

Figure 7. Comparison of cumulative mass loading curves for Indiana fly ash with and without Vicron sorbent added downstream.

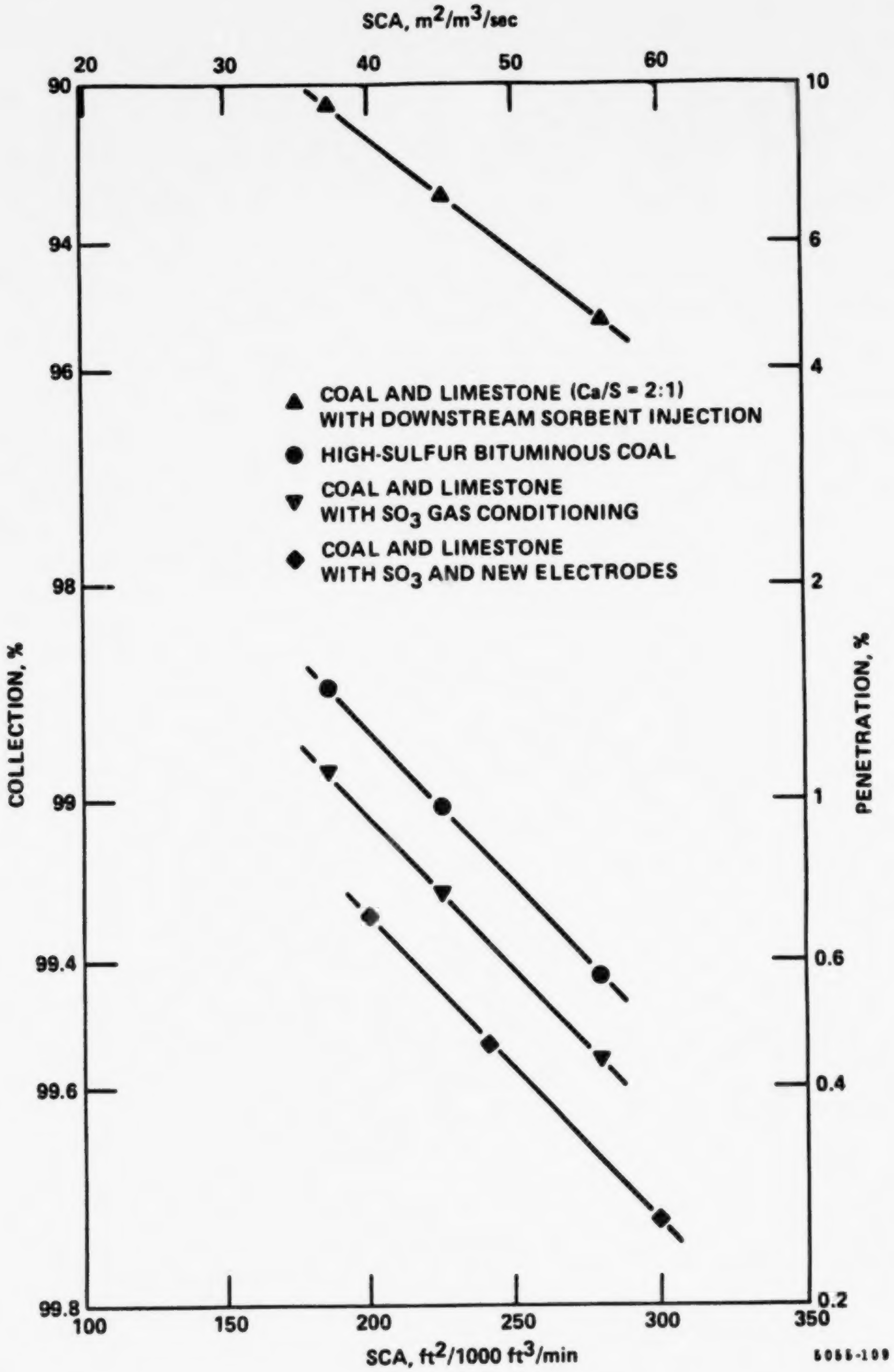

Figure 8. Results from ESP model simulation.

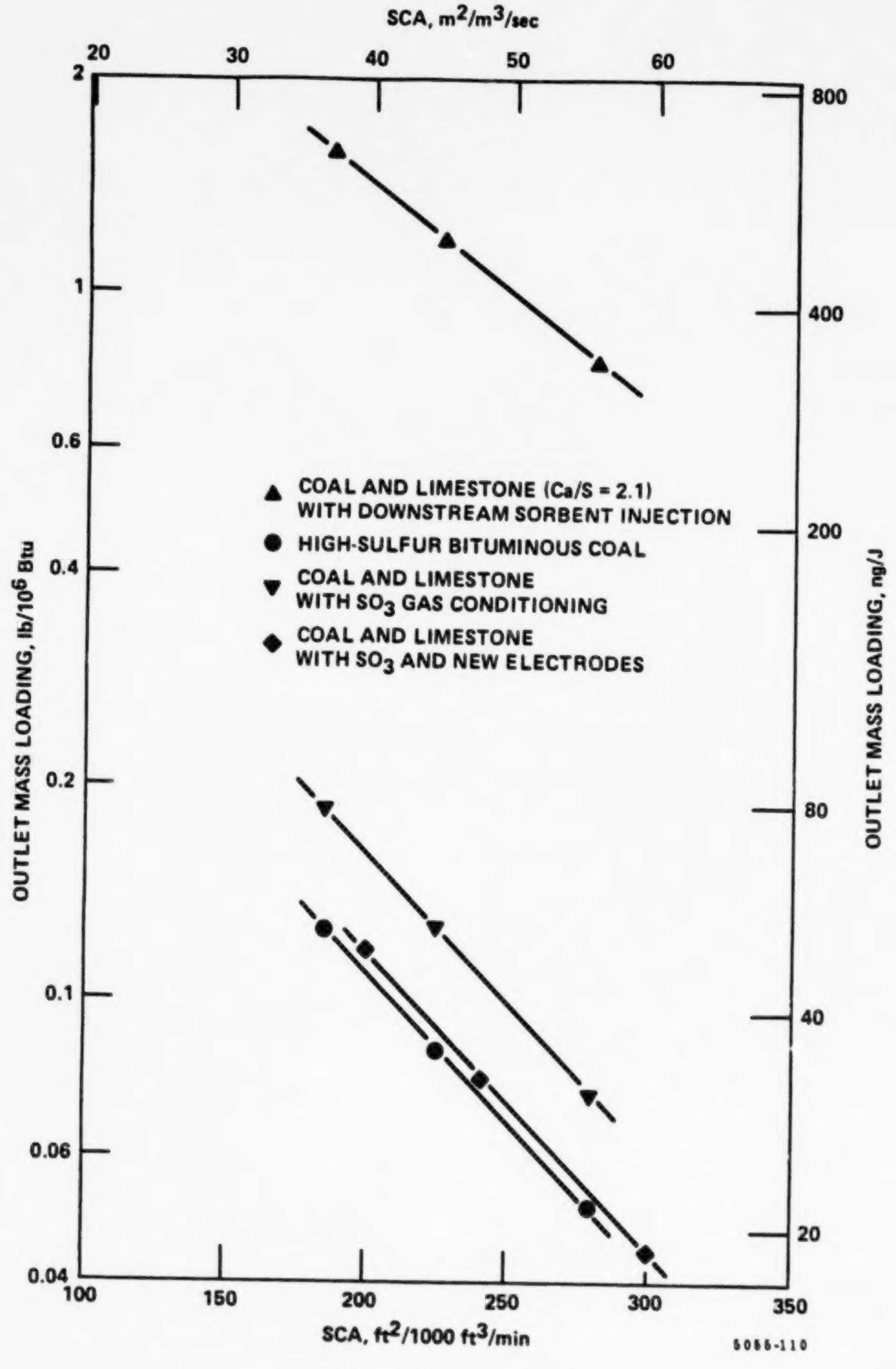

Figure 9. Calculated outlet mass loadings from ESP model simulation.

Table 1. System Design Temperatures and Gas Velocities

	Average gas temp, °C (°F)	Average velocity, m/sec (ft/sec)
Furnace	1621-1149 (2950-2100)	1.3 (4.2)
Simulated superheater/reheater	1149-943 (2100-1730)	7.0 (23)
Refractory-lined water jacket	943-829 (1730-1525)	20.1 (66)
Air preheater	829-477 (1525-890)	10.7 (35)
Heat exchanger No. 2	477-313 (890-595)	9.4 (31)
Air-cooled loops	313-183 (595-362)	18.3 (60)
Water-cooled loops	183-127 (362-260)	16.8 (55)

Table 2. Properties of Vicron Limestone and Longview Hydrated Lime[a]

	Vicron	Longview
Ca as $CaCO_3$, wt %	98.7	--[b]
Ca as $Ca(OH)_2$, wt %	--[b]	95.2
Surface area, m^2/g	0.82	16.6
Mass median diameter by sedimentation, μm	15	2.3

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a. Prior to furnace injection.

b. Not applicable.

Table 3. Proximate and Ultimate Analyses of Indiana 2.3% Sulfur Bituminous Coal

Proximate	Wt percent
Moisture	8.92
Ash	7.56
Volatile matter	34.23
Fixed carbon	49.29
Btu/lb	12,146
Sulfur	2.29

Ultimate	Wt percent
Moisture	8.92
Carbon	68.02
Hydrogen	4.42
Nitrogen	0.97
Chlorine	0.43
Sulfur	2.29
Ash	7.56
Oxygen[a]	7.39

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a. Oxygen determined by difference.

Table 4. Chemical Analyses of Fly Ash and Fly Ash/Sorbent Mixture Produced from Indiana Coal and Vicron Limestone

	Without Vicron, weight percent	With Vicron, weight percent
Li_2O	0.03	0.02
Na_2O	0.08	0.07
K_2O	0.59	0.35
MgO	0.19	0.44
CaO	0.28	39.4
Fe_2O_3	25.3	12.7
Al_2O_3	26.1	13.8
SiO_2	44.5	25.1
TiO_2	0.91	0.46
P_2O_5	0.07	0.03
SO_3	0.54	7.7

Table 5. Precipitator Mechanical Parameters

Three electrical sections in the direction of gas flow
Three baffled sections in the direction of gas flow
Gas sneakage per baffled section = 10%
Weighted wires in 22.9-cm (9-in.) ducts
Mean gas velocity = 1.52 m/sec (5.0 ft/sec)
Relative standard deviation of mean gas velocity = 0.25
Gas flow rate = 165 m^3/sec (350,000 ft^3/min)
Plate area per section = 2,434 m^2 (26,200 ft^2)
Specific collection area = 44.3 m^2/m^3/sec (225 ft^2/1000 ft^3/min)

Table 6. Precipitator Electrical Parameters

- High-sulfur bituminous coal
  Ash resistivity 2 x 10^{10} ohm cm at 149°C (300°F)

Section	kV	nA/cm^2
1	43	20
2	42	29
3	40	30

- Coal and limestone
  Ash resistivity 2 x 10^{12} ohm cm at 149°C (300°F)

Section	kV	nA/cm^2
1	30	0.8
2	29	1.2
3	30	2.5

- Coal and limestone, with SO_3 conditioning
  Ash resistivity 2 x 10^{10} ohm cm at 149°C (300°F)

Table 7. Precipitator Retrofit Parameters

- Flue gas conditioning with SO_3
  Ash resistivity 2 x 10^{10} ohm cm at 149°C (300°F)

- One precharging section, 0.61 m (2 ft) long,
  with 0.254 cm (0.1 in.) wires in 22.9 cm (9 in.) ducts
  Section: 45 kV, and 50 nA/cm^2

- Three collection sections,
  with 0.95 cm (3/8 in.) wires in 22.9 cm (9 in.) ducts
  Each section: 50 kV, and 10 nA/cm^2

EVALUATION OF TEMPERATURE HISTORIES IN THE RADIANT AND CONVECTIVE ZONES OF A PULVERIZED COAL-FIRED STEAM GENERATOR

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ABSTRACT

The effectiveness of in-situ desulfurization by direct injection of calcium-based dry sorbents is sensitive to the thermal environment in boilers. More specifically, the temperature histories of gases and sorbent particles in the radiant zone and the high-temperature convective pass sections play an important role in the sulfur capture process. Estimation of temperature histories requires a detailed description of the furnace heat transfer and flow field. This paper discusses the detailed field measurements of temperatures and velocities in a wall-fired utility boiler. The temperature measurements at full boiler load indicate that an assumed sulfation temperature window ($800 < T < 1200$ °C) starts close to the beginning of the high-temperature radiant superheater and extends to the back pass cavity. The residence times for the bulk flow in this temperature zone are approximately 1 second at full boiler load. At 60% load, the residence times are longer.

INTRODUCTION

Sulfur oxide emissions from large stationary combustion devices burning high sulfur containing fuels, such as coal and low grade oils, pose an environmental problem which is believed to be directly related to formation of acid rain in the U.S. and Canada(1). The conventional means of flue gas desulfurization involves the use of wet scrubbers. However, these devices are both capital and operating cost intensive and require considerable maintenance. Recently, other means of direct in-furnace desulfurization of combustion gases has been shown to be viable and potentially less expensive. This new technology involves the injection into the combustion chamber of pulverized calcium-based dry sorbents which absorb and react with the gaseous sulfur species in the furnace gases. In this process, two main steps are involved. These are thermal decomposition, often referred to as calcination(2,3) in the form

$$CaCO_3 \text{ (solid)} \rightarrow CaO \text{ (solid)} + CO_2 \text{ (gas)}, \qquad (1)$$

and sulfation(4) which overall can be represented by

$$SO_2 \text{ (gas)} + CaO \text{ (solid)} + 1/2\ O_2 \text{ (gas)} \rightarrow CaSO_4 \text{ (solid)} \qquad (2)$$

The $CaSO_4$ particulate can be removed with the existing particulate removal systems such as cyclones, baghouses, and electrostatic precipitators. This technology, often referred to as LIMB (for Limestone Injection with Multistage Burners), is intended primarily as a retrofit technology. The two steps of the process, calcination and sulfation, have been shown to be highly sensitive to the time-temperature profiles experienced by the sorbent.(5) For instance, the sorbent reactivity is strongly dependent on the peak temperature experienced by the sorbent particles, and the sulfation kinetics has been found, from bench-scale studies(6), to be most favorable in the overall temperature zones between 800 and 1200°C. Therefore, effective implementation of the process in boilers requires knowledge of the temperature field and the temperature histories in a boiler to maximize sorbent utilization. This can be achieved by detailed experimental characterization of thermal environment and flow field in field operating boilers. However, such an approach would be difficult, time consuming and expensive. Alternatively, a predictive methodology, tested against field data for representative sample boilers of most common types, would provide a more attractive solution. This predictive methodology could be used to study the thermal environments and flow fields in many different boilers to assess the potential for LIMB application. Currently, an EPA funded program is underway to study the adequacy of a predictive approach for evaluation of thermal and flow characteristics in boilers. The main objectives of this study are to:

- Review the available furnace thermal prediction methodologies and flow models and to select the prediction method most suitable for evaluation of temperature and flow fields in boilers(7).
- Conduct field tests at the two most common type boilers (wall-fired and tangentially fired) and compare the test data with the predictions of the selected methodology.
- Determine the adequacy and accuracy of such an approach for future predictive evaluations.

The review of predictive methodologies and the field tests at two boilers have been completed. These boilers are the wall-fired unit of Duck Creek Power Station near Canton, Illinois, owned and operated by Central Illinois Light Company, and the tangentially fired boiler unit 5 of Conesville Generating Station in Conesville, Ohio, owned and operated by American Electric Power Company. The detailed results of the field tests will be published in separate EPA reports. This paper summarizes the field tests conducted at the wall-fired unit.

EXPERIMENTAL

Test Boiler

The field tests reported here were conducted at the wall-fired boiler of Duck Creek Power Station located near Canton, Illinois. The test boiler is a front-wall fired Riley unit. The general arrangement of the boiler is shown in Figure 1. The boiler is coupled with a generator producing 420 MW_e electrical output at full boiler load. The boiler characteristics are listed in Table 1. The furnace is 11.6m (38ft) deep and 16.8m (55ft) wide in the burner area. The 24 burners, arranged in 4 horizontal rows of 6 burners each, supply the fuel to the furnace. The coal is pulverized in 3 Riley ball-type pulverizers each supplying 8 burners. The steam generator is a natural circulation boiler with superheat and reheat steam cycles. It is designed to produce 1,363,600 kg/hr ($3x10^6$ lb/hr) steam at 178 atm (2600 psig) and 540°C (1005°F). The burners installed at this unit are low-NO_x Controlled Combustion Venturi (CCV) burners(8).

The coal fired at this unit is received from the Crown II mine in Illinois on a long term contract. A typical proximate and ultimate analysis and heating value of the coal are listed in Table 2. These values did not vary by more than 20% during the test period. The coal is a high volatile bituminous - C coal. The coal fineness varied between 73 and 85% by mass through 200 mesh screens (74 micron mean size).

Test Objectives and Operating Conditions

The primary test objective was to provide the necessary test data on the furnace thermal environment and flow field for comparison with the predictions of a furnace heat transfer/flow model. In addition, the location of the sulfation temperature window and the residence times in this zone can be evaluated from the test data. This paper reports the furnace gas temperature and velocity measurements made at the full boiler load. Comparison with the low load (approximately 60% of full load) operation of the boiler is also presented. At 60% load, one of the pulverizers supplying the top row of six burners and the two middle burners on the next row was out of service. This is the base load at which the unit operates during low power demand hours. Tests conducted at this load allow comparisons of the changes in the boiler thermal environment due to the different firing configuration and the reduced firing rate. The temperature measurements included traverses made in various planes throughout the radiant furnace and the upper portion of the convective back pass since the region of interest for the LIMB process extends to temperatures down to 800°C. Some of the monitored input/output parameters are listed in Table 3 for 100% and 60% loads.

Due to the large number of measurements, completion of each test condition required several days of testing. This necessitated a careful investigation of the long-time transients (daily and between soot blowing cycles) in the thermal environment because of the soot blowing and variations in the boiler input conditions. A preliminary evaluation, based on the measurements of the radiant furnace exit temperatures and calculations in the convective back pass, revealed that the temperature variations due to soot blowing were small. In fact, it was observed during the tests that the radiant furnace walls were clean, with only thin powdery deposits. Therefore, no soot blowing took place in the radiant furnace. In the back pass, the flue gas temperatures varied by 10-15°C over the soot blowing cycle. These fluctuations were small and did not justify the coordination of the measurements with the soot blowing cycle. The variations in the input parameters were also kept within prespecified limits.

Measurement Techniques And Locations

Gas temperatures were measured with conventional water-cooled suction pyrometer probes. A few velocity measurements were also made with two-hole impact probes to determine the magnitude and direction of the velocity vector in the plane perpendicular to the probe axis. During the tests, other measurements included local and economizer outlet species concentrations, radiative heat flux measurements and particulate size distributions. The test equipment and measurement procedures are described in detail (9).

It should be pointed out that in-furnace temperature and velocity measurements are difficult in a large coal-fired boiler since the furnace environment is extremely hostile and sampling at distances up to 8m (26ft) into the furnace is generally required. The accessible locations adequate for probe insertion are also major constraints in making in-furnace measurements. In general, all boilers are equipped with furnace observation ports located near the furnace corners. Sometimes even these locations are obstructed, by the equipment outside the boiler, for adequate insertion depths into the furnace with probes. All these problems and constraints required sampling with several probes with lengths varying from 3m (10ft) to 7.6m (25ft). In areas of major interest, some wall soot blowers were removed for additional access into the furnace. Because of the interest in the upper convective back pass, sampling ports were also installed in this area. The following section highlights some of the results obtained during these field tests.

RESULTS

Figure 2 shows the temperature measurements made in the radiant furnace. The maximum temperature of 1539°C was measured in the region above the fourth burner row. The temperatures along the back wall at lower elevations were made beyond the tails of the flames and were somewhat lower. However, side-to-side variations in the temperature levels were observed. In the zone above the nose, in the vicinity of the pendant radiant superheaters, the gas temperatures start to decline gradually. However, the gas temperatures in the central portion of the boiler are still above 1200°C at Z equals 37.9m. At the uppermost sampling elevation (Z equals 44.7m) where the flow starts to bend toward the screen tubes, the temperatures were cooler, but still higher than 800°C. Some variations in the temperature levels across the furnace width were still present. The temperature measurements were continued in the back pass until the temperature levels dropped below 600°C. These measurements are shown in Figure 3. The two uppermost locations would have the most representative temperatures at those locations; whereas, the other sampling locations were unfortunately either too close to the water walls or in the recirculation zone behind the screen tubes. In the back pass, the gas temperatures drop fairly quickly to 700°C.

Based on these temperature measurements, the approximate location (upper and lower boundaries) of the assumed temperature window ($800 < T < 1200°C$) can be estimated. Figure 4 shows this zone in the boiler for full load and 60% load.

Since the potential interest from the LIMB application viewpoint lies in this region of the boiler, velocity measurements were made there to evaluate the residence times. The average vertical (Z-direction) components of the velocity vector at the two elevations (Z equals 37.9m and 44.7m) are shown in Figure 5. It should be noted that the measured velocities, in general, agree with the plug flow velocity values ($\bar{V}_Z$) calculated based on the furnace throughput rate, estimated average gas temperature at that elevation, and the cross sectional area. Some variations in the velocity across the furnace depth at the highest elevation are observed. This is the region where the flow is bending toward the screen tubes to enter the back pass. In this region, and in the recirculation zone behind the screen tubes, it is difficult to determine the velocities and the residence times. However, it is possible to estimate the temperatures and residence times based on measurements and calculations assuming that the X component of the velocity is negligible. This assumption holds in the regions between the pendant superheaters.

Because of the cooler temperatures close to the walls and some asymmetry in the temperatures across the furnace width, four sections denoted by 1,2,3, and 4 shown in Figure 4 were chosen for time-temperature calculations. Based on the average measured vertical velocities in these slices, as shown in Figure 5, the mass flow distribution corresponds to 12,36,32, and 20% of the total mass flow in slices 1,2,3 and 4, respectively. Figure 6 shows the time-temperature profiles for these four slices. The time starts from elevation Z equals 35.7m (117 ft), labeled in Figure 5. At this elevation, all the temperature levels with the exception of the fourth slice are above 1200°C. For the two center sections (2,3) through which 68% of the total mass flows, the residence times in the temperature zone (800°C $<T<$ 1200°C) are about 1 second. In section 1, the residence time in the same temperature window is about 1.6 seconds; whereas, the residence time for section 4 appears to be relatively shorter. Finally, Figure 7 shows the bulk mass-mean time-temperature relationship for the full and the 60% boiler loads. Although the temperature levels at 60% load are lower initially, compared to the full load temperature levels, the residence times are longer due to the reduced furnace throughput. The combined result is somewhat longer residence times in the sulfation temperature window. The beginning of this zone is upstream of that for the full load.

CONCLUSIONS

The results of the field tests conducted at this particular wall-fired boiler suggest that:

- The temperature zone which is most conducive to sulfation reactions (800° $<T<$ 1200°C) is located in the upper radiant furnace starting in the vicinity of the pendant superheaters.
- The residence times in this temperature window are on the order of a second.
- At approximately 60% load, the high temperature end of this zone shifts slightly upstream of that for the full load, and the residence times are greater than 1 second.

ACKNOWLEDGMENTS

This work was conducted under United States Environmental Protection Agency (EPA) Contract 68-02-3927. Riley Stoker was a major subcontractor to Energy and Environmental Research Corporation (EER). The authors are pleased to acknowledge the contributions of B. A. Folsom as EER's program manager. The participation of C. E. McHale and T. Semolynas of Riley Stoker Research and the cooperation of the Duck Creek Power Station personnel during these field tests are also greatly appreciated.

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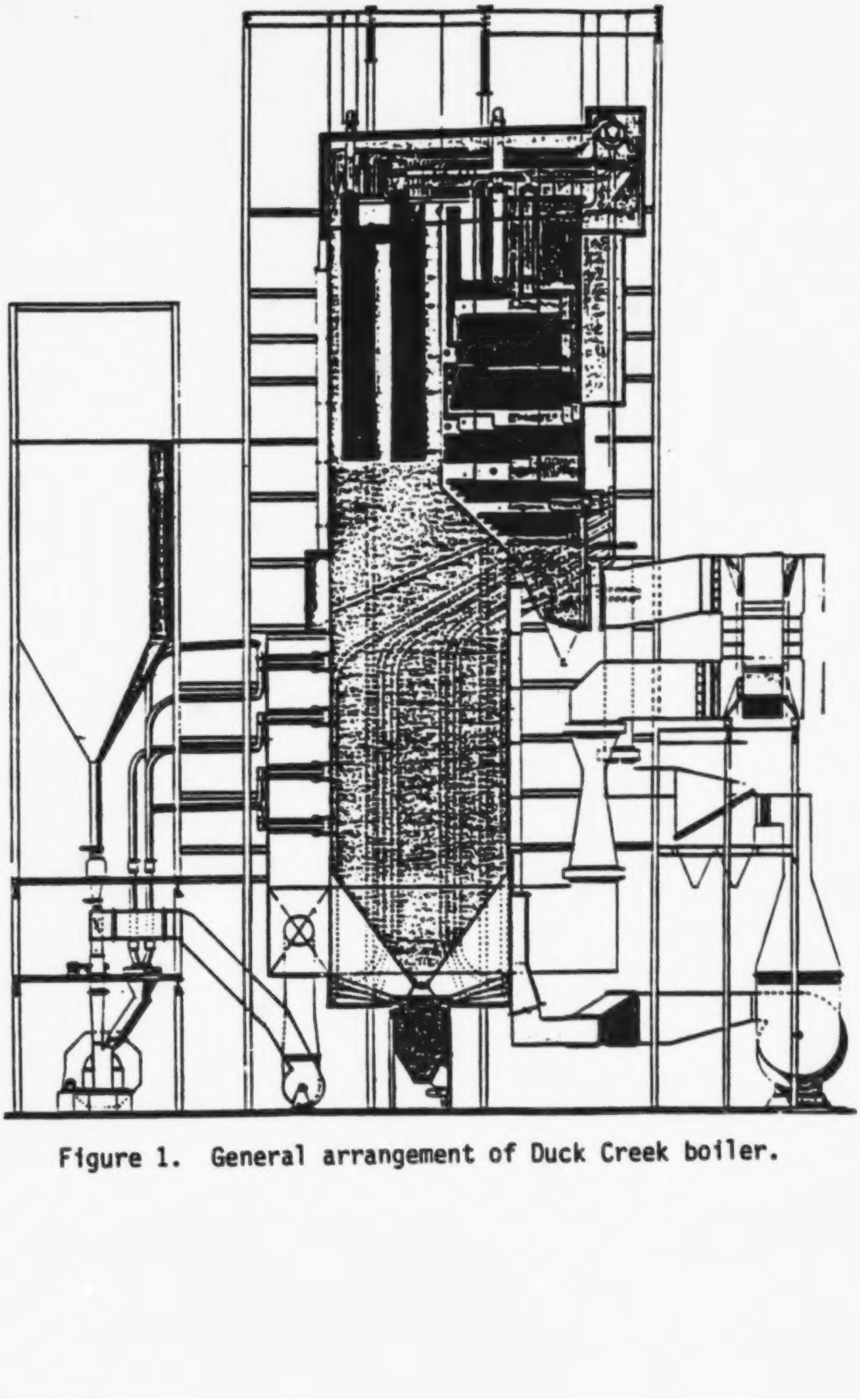

Figure 1. General arrangement of Duck Creek boiler.

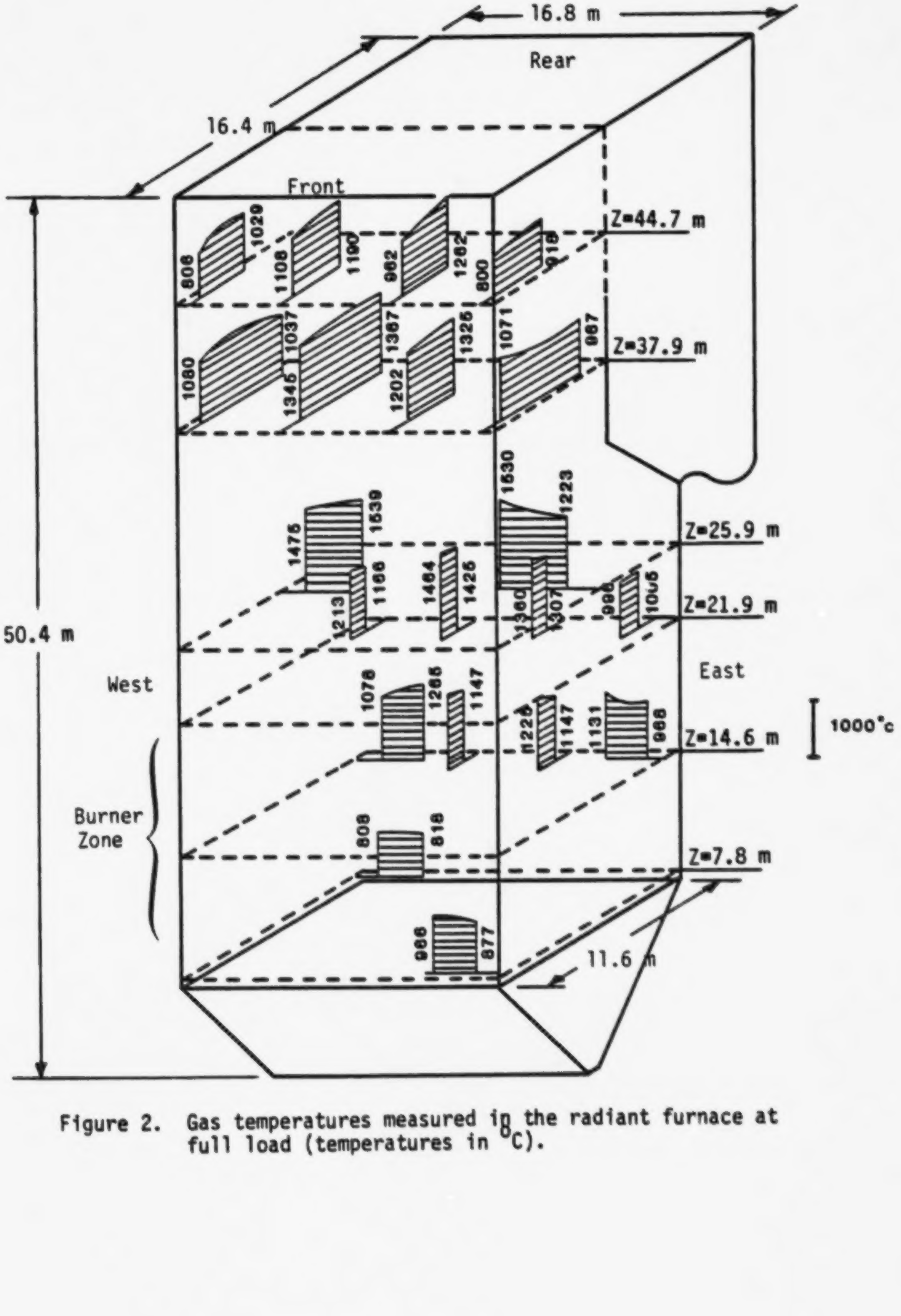
16.8 m
Rear
16.4 m
Front
Z=44.7 m
808
1029
1108
1190
962
1262
800
918
Z=37.9 m
1080
1037
1345
1367
1202
1326
1071
967
1630
1223
1475
1539
Z=25.9 m
1213
1166
1464
1426
1360
1307
998
1006
Z=21.9 m
50.4 m
West
East
1078
1265
1147
1228
1147
1131
968
Z=14.6 m
1000°c
Burner Zone
808
818
Z=7.8 m
966
877
11.6 m

Figure 2. Gas temperatures measured in the radiant furnace at full load (temperatures in °C).

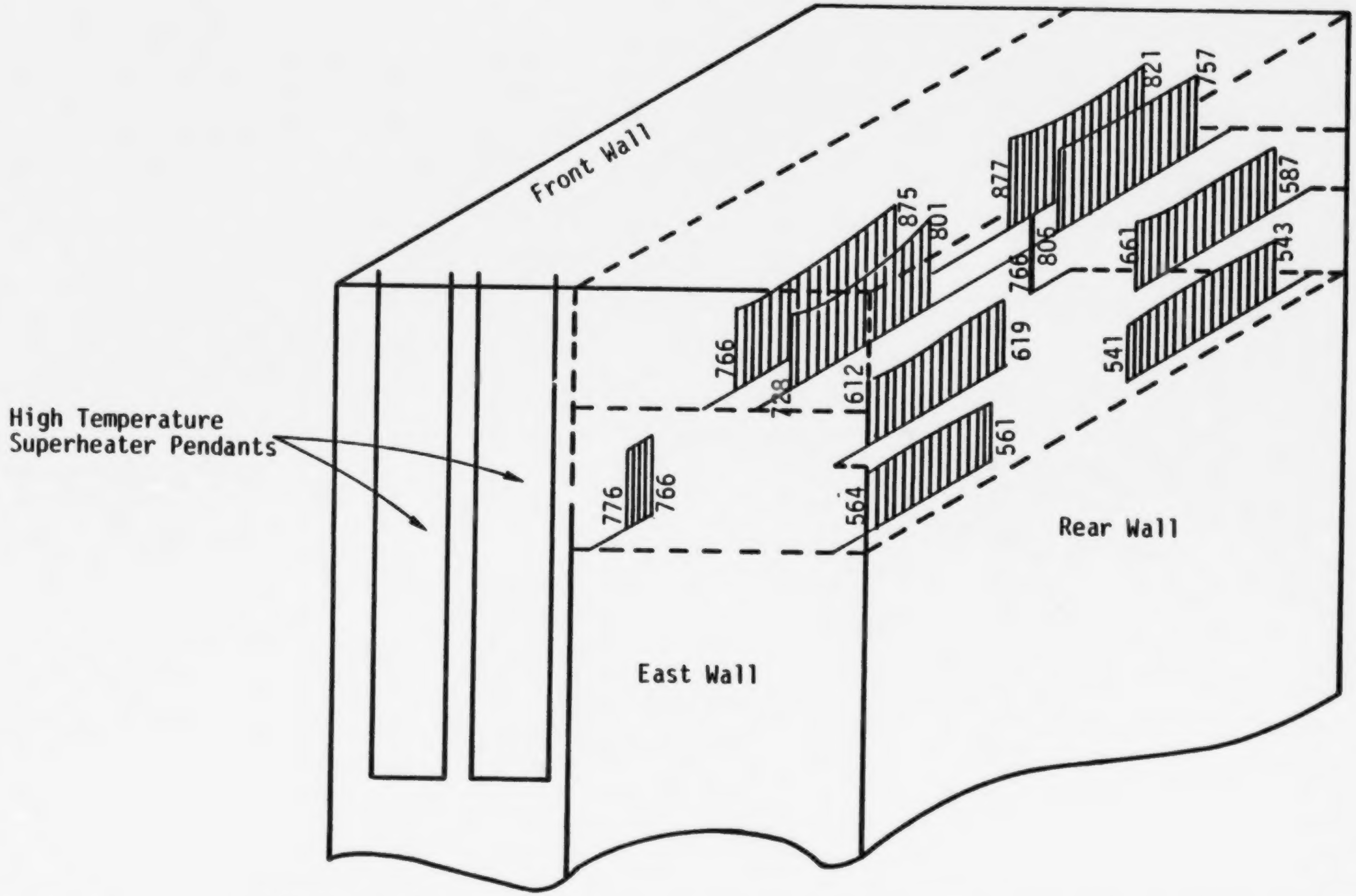
Front Wall
High Temperature
Superheater Pendants
776
766
766
728
612
564
875
801
619
561
877
766
806
821
757
661
587
541
543
Rear Wall
East Wall

Figure 3. Gas temperatures measured in the convective back pass at full load (temperatures in ^{0}C).

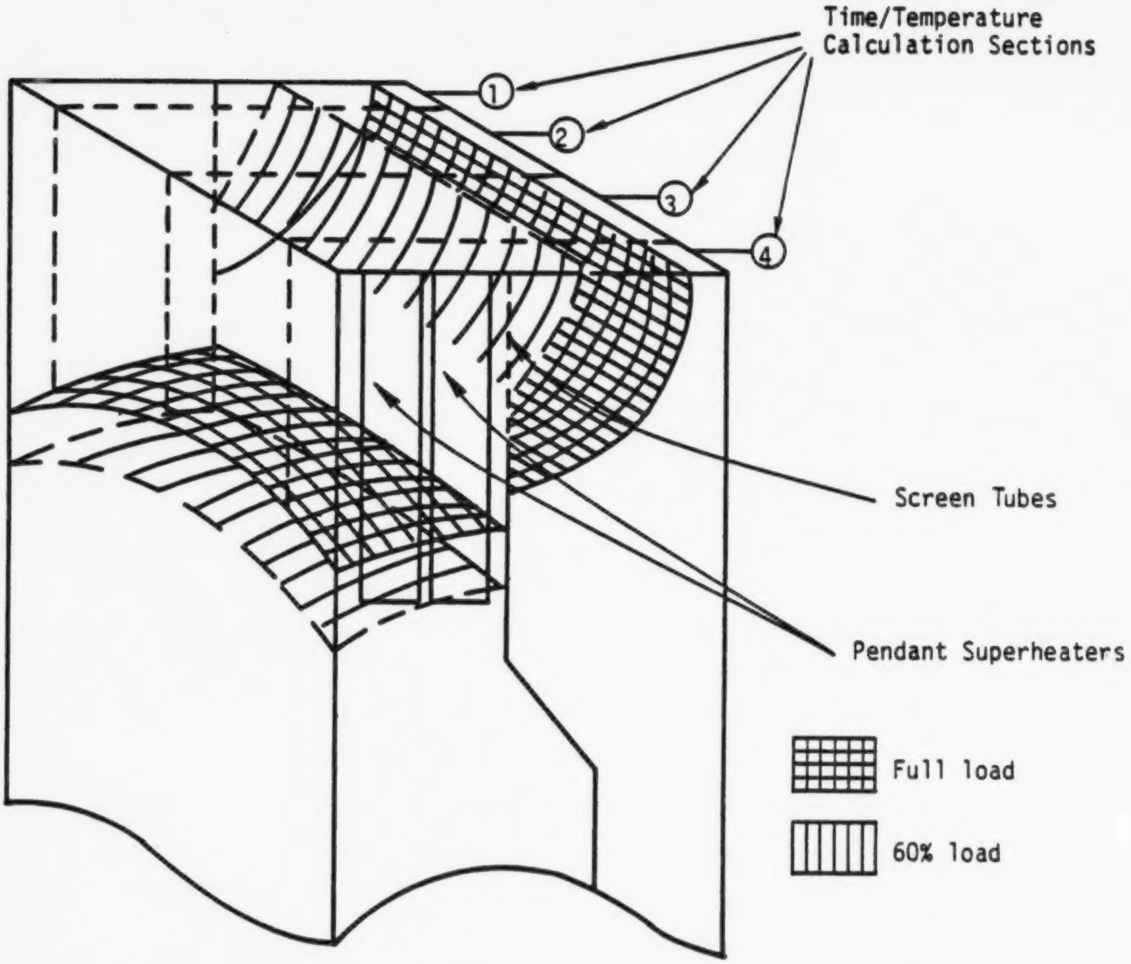
Time/Temperature
Calculation Sections
①
②
③
④
Screen Tubes
Pendant Superheaters
Full load
60% load

Figure 4. Approximately location of 800 T 1200°C temperature zone in the boiler.

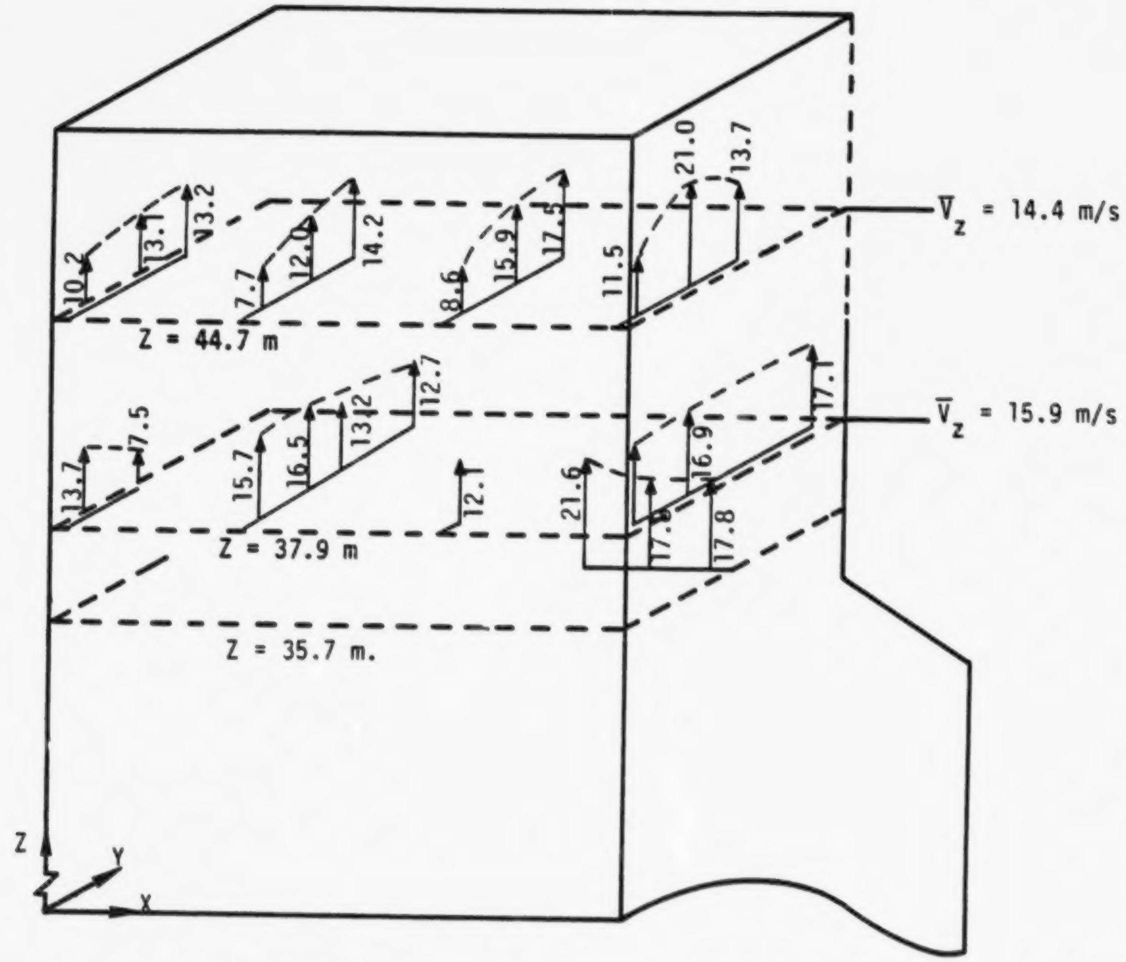
10.2
13.1
13.2
7.7
12.0
14.2
8.6
15.9
17.5
11.5
21.0
13.7
$\overline{V}_z$ = 14.4 m/s
Z = 44.7 m
13.7
7.5
15.7
16.5
13.2
12.7
12.1
21.6
17.8
17.8
16.9
17.1
$\overline{V}_z$ = 15.9 m/s
Z = 37.9 m
Z = 35.7 m.
Z
Y
X

Figure 5. Measured velocities in the upper radiant furnace (all velocities in m/s).

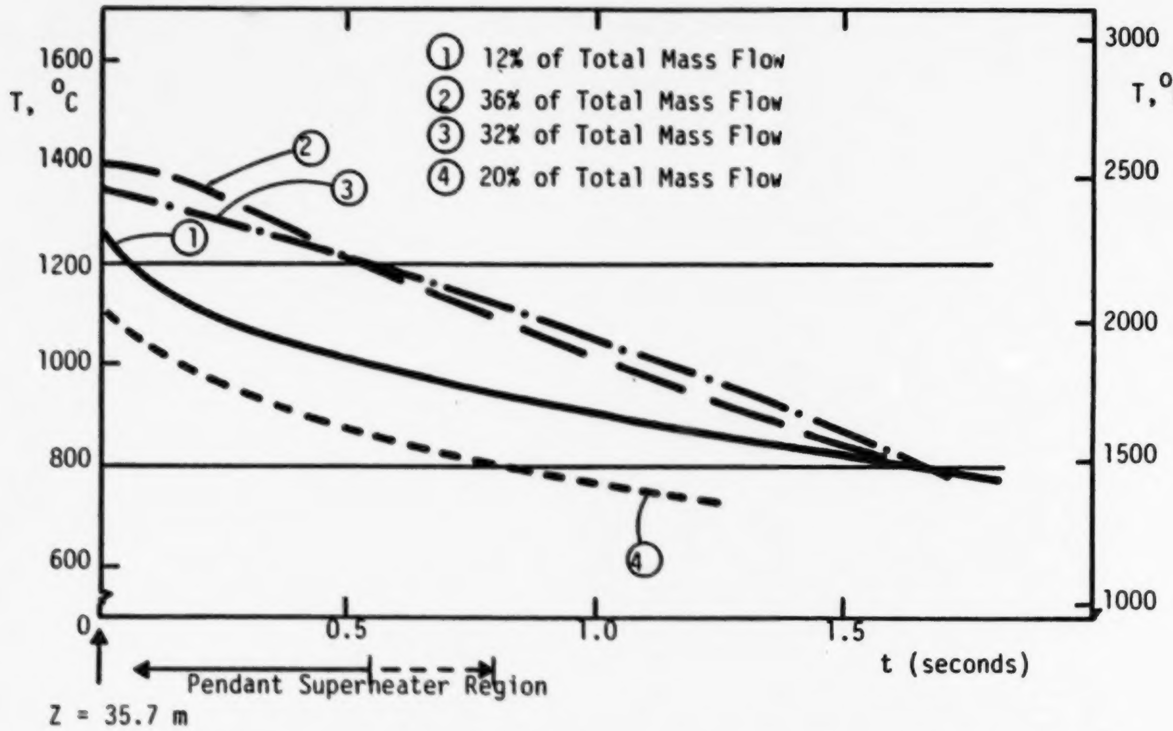

Figure 6. Temperature histories in the upper furnace at full load.

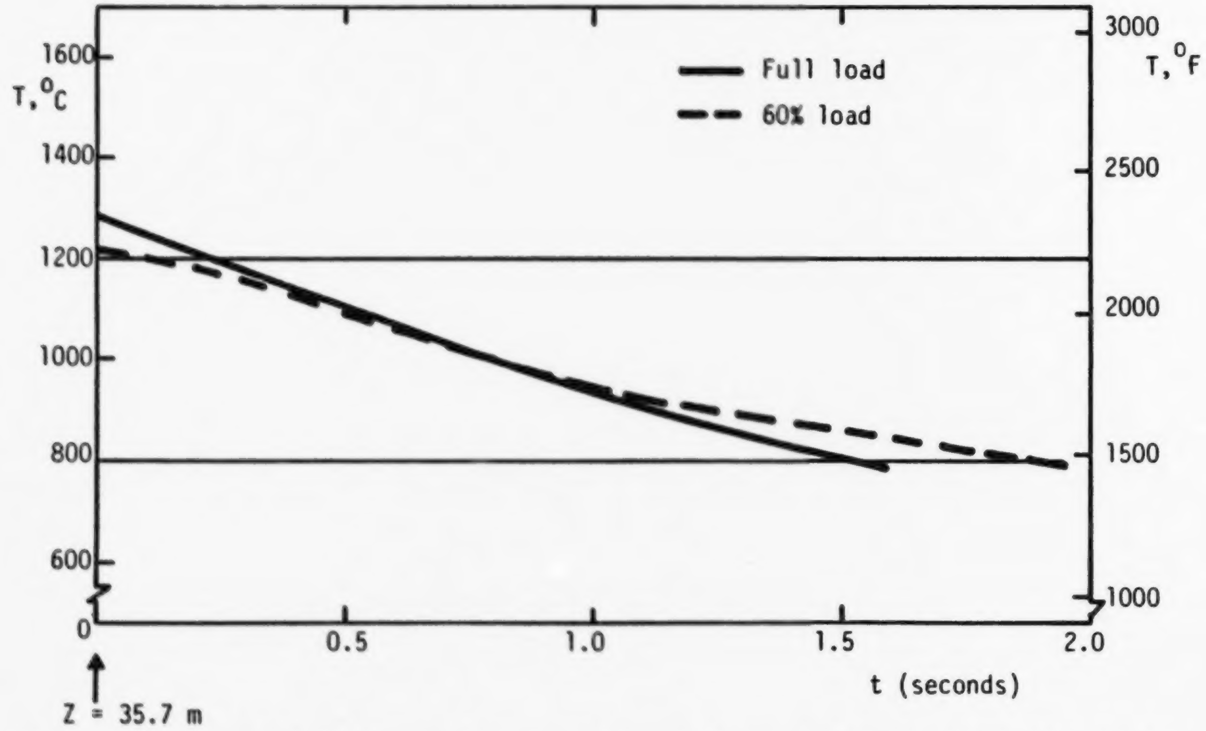

Figure 7. Averaged bulk temperature - residence times at full and 60% boiler loads.

Table 1

DUCK CREEK BOILER CHARACTERISTICS

Parameter	Value
Firing	
Configuration	Front-wall fired
Firing Rate	1250 MW_{th} (4.27×10^9 Btu/hr) full load
Pulverizers	3 Riley Ball-Type
No. of Burners	24
Rows	4
Burners per row	6
Dimensions	
Firing Depth	11.6 m (38 ft)
Width	16.8 m (55 ft)
Depth above nose	7.3 m (24 ft)
Knuckle to Nose Height	21.5 m (70.5 ft)
Nose Angle	48^o
Hopper Angle	55^o
Total Vertical Height	50.4 m (165 ft)
Thermal Environment	
Heat Release/Cooled surface	0.66 MW/m^2 (2.04×10^5 $Btu/hr\text{-}ft^2$)*
Heat Release/Volume	0.41 MW/m^3 (3.87×10^4 $Btu/hr\text{-}ft^3$)**

---

* In the radiant furnace below the pendants at full load.

** In the burner zone at full load.

Table 2

DUCK CREEK COAL ANALYSES

Proximate Analysis (dry):	Volatiles	40.5%
	Fixed C	49.6%
	Ash	10.9%
Ultimate Analysis (dry):	C	69.6%
	H	5.0
	N	1.3
	S	3.9
	Ash	10.9
	O	9.3

Moisture: 16.6%

Heating Value (dry): 29.20 MJ/kg (12,580 Btu/lb)

Table 3

INPUT/OUTPUT PARAMETERS

Parameter	100% Load	60% Load
Burners in Service	24	16
Electrical Load, MW_e	360-385	230-235
Excess O_2, % dry	3.5-4.0	3.3-3.8
Coal Flow Rate, tons/hr	145-155	91-95
Primary Air-Coal Temperature, °C	55	51-55
Windbox Air Temperature, °C	316-324	279-285
Primary Steam Flow, tons/hr	1140-1180	690-750
Superheat Steam Temperature, °C	535-541	500-540
Drum Pressure, atm	168-177	164-176
Drum Pressure, psig	2460-2590	2400-2575

IMPACT OF SORBENT INJECTION ON POWER PLANT HEAT RATES

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ABSTRACT

In-furnace SO_2 control via sorbent injection impacts boiler performance as a result of heats of reaction of chemical processes and increased auxiliary power demands. In addition, dry injection may effectively reduce flue gas acid dew points and thereby permit low-level heat recovery. This paper summarizes the effects of the chemical reactions and quantitatively evaluates the potential for heat rate improvement through supplemental heat recovery.

INTRODUCTION

As illustrated in Figure 1, there are a variety of alternative process configurations and sorbents for in-furnace SO_2 control. For the purposes of this analysis, the thermal effects of external (to the boiler) calcination, hydration, and pulverization were not included. Rather, the effect on boiler efficiency of calcination/dehydration and sulfation witin the boiler were quantified. These calculations were performed for the several sorbents as listed in Figure 2. In this context, the sorbents were assumed to be injected into the main furnace cavity wherein calcination occurs. In the calcination process, which is endothermic, carbon dioxide and/or water vapor evolves and calcium oxide (lime) results. A portion of the lime reacts with SO_2, which is an exothermic reaction, to form calcium sulfate. These reactions are illustrated in Figure 3.

In addition, SO_3 formed in the combustion process will be absorbed by the calcium byproducts. The removal of SO_3 provides an opportunity for operation of post boiler equipment at temperatures below typical acid dew point constraints. Since a 40°F decrease in stack gas outlet temperature is worth approximately 1 percent in boiler efficiency, in-furnace sorbent injection will facilitate improvements in power plant heat rates.

ANALYTICAL METHODOLOGY

Boiler efficiency calculations were performed based on standard combustion calculations for a hypothetical unit.(1) A simple computer model was constructed for this purpose. Calculations were perfomred for three coals as listed in Figure 4. The baseline conditions were for no sorbent injection, 300°F outlet flue gas temperature, 2 percent loss on ignition of the flyash, and 20 percent excess air. For Illinois no. 6 coal, the baseline boiler efficiency was 88.16 percent.

Similar calculations were then performed in which the calcination and sulfation reactions were incorporated in the computation. For this purpose, the heats of formation and heats of reactions (Figures 5 and 6) were built into the model. In addition, assumed SO_2 removal efficiencies for each sorbent as a function of calcium-to-sulfur molar ratio were factored into the analysis. The net effect of sorbent injection upon boiler efficiency was determined by comparison to computations for baseline conditions.

RESULTS AND DISCUSSION

The net effect on boiler efficiency and heat rate for the calcination and sulfation reactions is shown in Figure 7 for Illinois no. 6 coal. It can be seen that the net effect is not signficant; typically less than 0.3 percent for most conditions. This is primarily due to the balancing of exothermic and endothermic reactions which occur in the boiler. At low Ca/S ratios and for lower sulfur coals, the net effect would be typically less than 0.2 percent.

In general, the carbonates resulted in a net decrease in boiler efficiency and the hydroxides and free lime resulted in a net increase. This beneficial heat rate impact for the calcium hydroxide an/or lime will help offset higher costs for this material as compared to limestone.

All of the dolomitic materials wil produce a net decrease in boiler efficiency. This is due to the energy requirements for calcination/dehydration of the magnesium compound without a commensurate sulfaction reaction occurring. In Figure 8, the detrimental effect on boiler efficiency is illustrated for dolomitic carbonates and hydrates as a function of magnesium content. It can be seen that a 50 percent Mg sorbent will reduce boiler efficiency by about 0.1 percent more than an equivalent sorbent with no Mg.

The effect of lowering stack gas temperature (due to SO_3 removal) on boiler efficiency is shown in Figure 9. If the flue gas sensible heat can be utilized within the boiler (air, feedwater or sorbent preheating), reducing the stack gas temperature by 150°F will result in a nominal 4 percent improvement in boiler efficiency. As shown on Figure 10, each 40°F increment in flue gas temperature reduction will result in 1 percent improvement in boiler efficiency and 100 (Btu/kWh) decrease in unit heat rate. The fuel cost impact for this level of heat rate improvement is very site-specific, but would be substantial and attractive for most power plants.

There are other impacts of sorbent injection on unit heat rates, including: auxiliary power requirements for sorbent preparation and conveying, increased sootblowing, auxiliary power for handling and disposal of increased solids in the boiler and electrostatic precipitator, onsite external calcination and/or hydration, and redistribution of heat transfer within the boiler. The magnitude of the combined effect of these impacts is very site-specific. However, it is estimated that it may result in a 1 to 2 percent decrease in unit heat rates.

CONCLUSIONS

1. Net calcination/sulfation energy requirements do not significantly affect boiler efficiency. At anticipated Ca/S ratios, it is typically less than 0.2 percent.

2. CaO and $Ca(OH)_2$ result in net increases in boiler efficiency; $CaCO_3$ and dolomitic sorbents result in net decreases.

3. Increases in calcium utilization result in increases in boiler efficiency.

4. Flue gas temperature reductions (and heat recovery) are possible due to SO_3 removal; this provides a significant opportunity for heat rate improvements.
5. Site-specific design factors will increase the auxiliary power requirements for furnace sorbent injection independent of calcination/sulfation effects.

REFERENCES

1. Babcock & Wilcox, STEAM Its Generation and Use, 38th Edition, 1972.
2. Hodgman, C. D. et al., Handbook of Chemistry and Physics, The Chemical Rubber Publishing Co., 44th Edition, 1963.

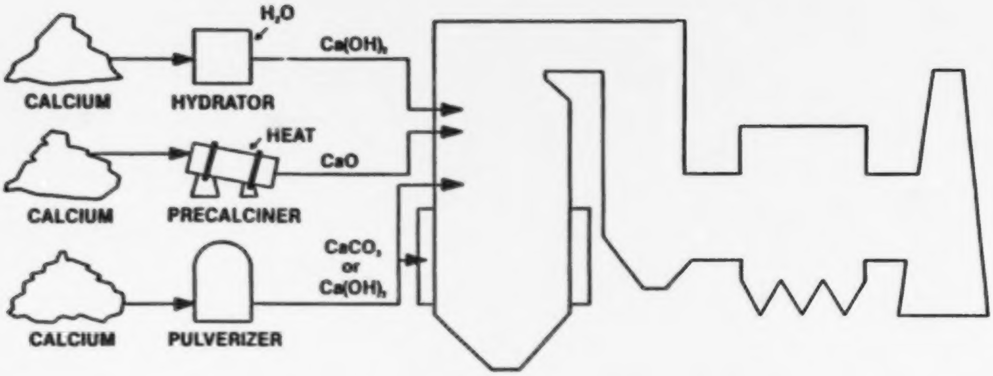

H_2O
$Ca(OH)_2$
CALCIUM
HYDRATOR
HEAT
CaO
CALCIUM
PRECALCINER
$CaCO_3$
or
$Ca(OH)_2$
CALCIUM
PULVERIZER

Figure 1. Sorbent Injection Alternatives

LIMESTONE:	**$CaCO_3$**
DOLOMITE:	**$CaCO_3MgCO_3$**
CALCIUM HYDROXIDE: **(HYDRATED LIME)**	**$Ca(OH)_2$**
DOLOMITIC HYDROXIDE: **(PRESSURE HYDRATED LIME)**	**$Ca(OH)_2Mg(OH)_2$**
LIME: **(PRECALCINED)**	**CaO**

Figure 2. Dry Sorbent for Furnace Injection

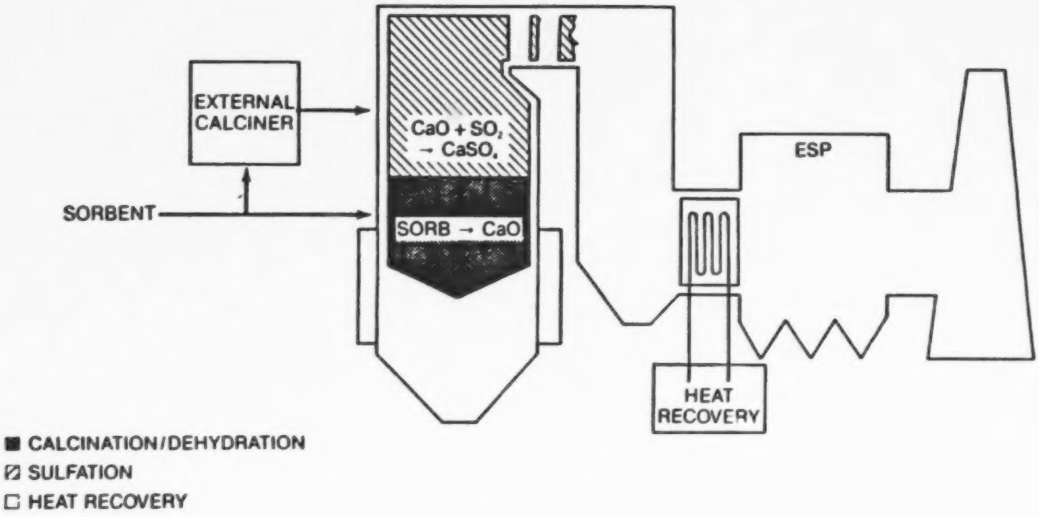

EXTERNAL CALCINER
SORBENT
$CaO + SO_2 \rightarrow CaSO_4$
SORB → CaO
ESP
HEAT RECOVERY
■ CALCINATION/DEHYDRATION
▨ SULFATION
☐ HEAT RECOVERY

Figure 3. Sorbent Injection Heat Rate Impacts

	Powder River Basin	Appalachian Medium Sulfur	Illinois No. 6
Carbon (% by wt.)	47.85	69.7	57.5
Hydrogen "	3.40	4.9	3.7
Sulfur "	0.48	2.0	4.0
Oxygen "	10.82	8.1	5.8
Nitrogen "	0.62	1.3	0.9
Moisture "	30.4	6.0	12.0
sh "	6.43	8.0	16.1
ating Value (Btu/lb)	8,020	13,400	10,100
($/10⁶ Btu)	1.59	2.32	1.89

Figure 4. Coals

	(Btu/lb-mole)
Ca	0
CaO	− 273,420
$CaCO_3$	− 519,300
$Ca(OH)_2$	− 424,440
$CaSO_4$	− 616,320
Mg	0
MgO	− 258,840
$MgCO_3$	− 478,800
$Mg(OH)_2$	− 397,800
H_2O	− 104,040
CO_2	− 169,290
SO_2	− 127,730

Figure 5. Heats of Formation

	△HR (Btu/lb-mole)
$CaCO_3 \rightarrow CaO + CO_2$	+ 76,590
$Ca(OH)_2 \rightarrow CaO + H_2O$	+ 46,980
$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4$	− 215,172
$MgCO_3 \rightarrow MgO + CO_2$	+ 50,670
$Mg(OH)_2 \rightarrow MgO + H_2O$	+ 34,920
$CaCO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + CO_2$	− 138,582
$Ca(OH)_2 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + H_2O$	− 168,192

NOTE: − HR DENOTES AN EXOTHERMIC REACTION.

Figure 6. Calcination/Sulfation Reactions

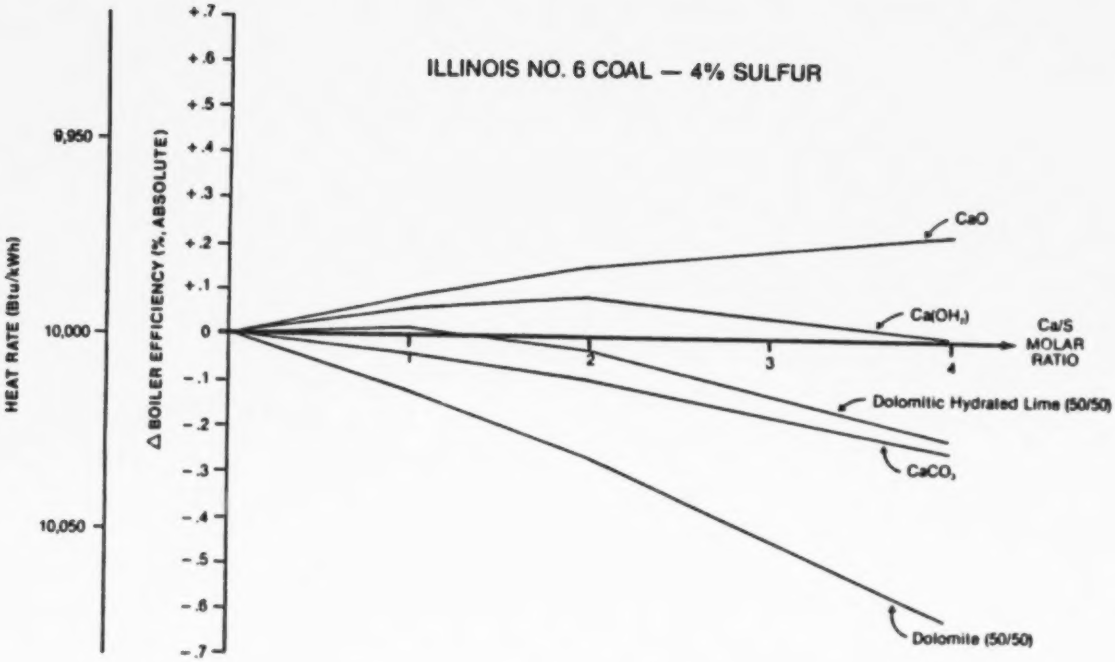


Figure 7. Net Effect on Boiler Efficiency and Heat Rate for Calcination and Sulfation Reactions

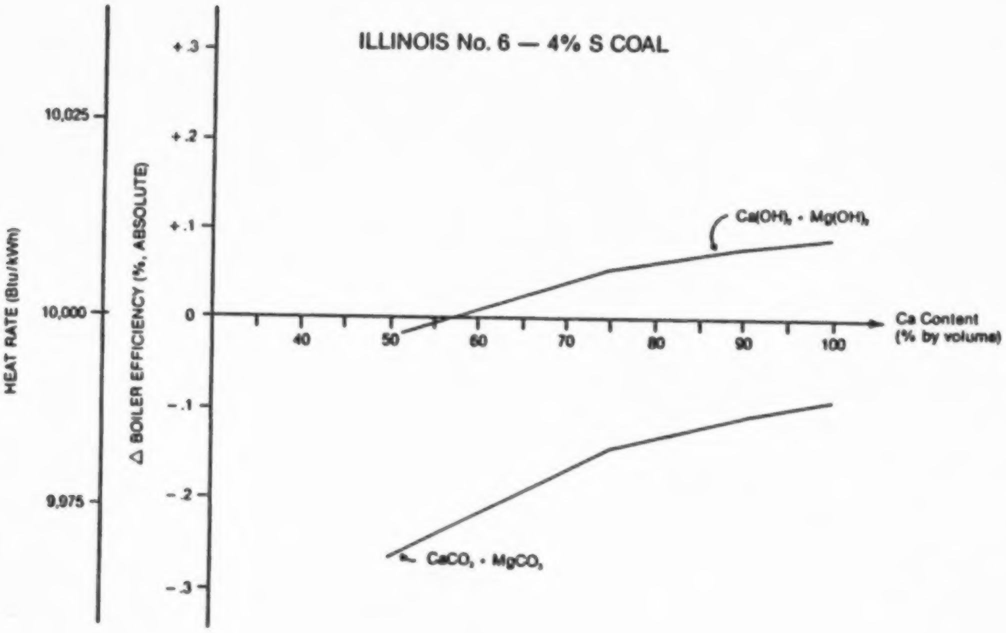


Figure 8. Net Effect on Boiler Efficiency and Heat Rate For Dolomitic Sorbents of Varying Mg Content

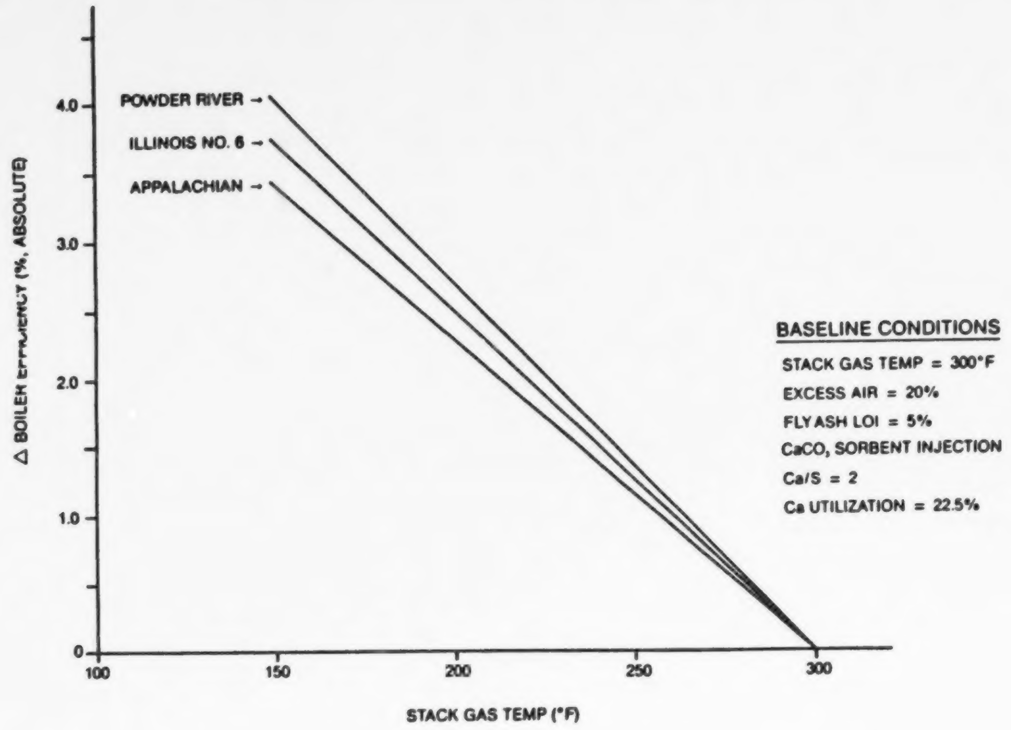
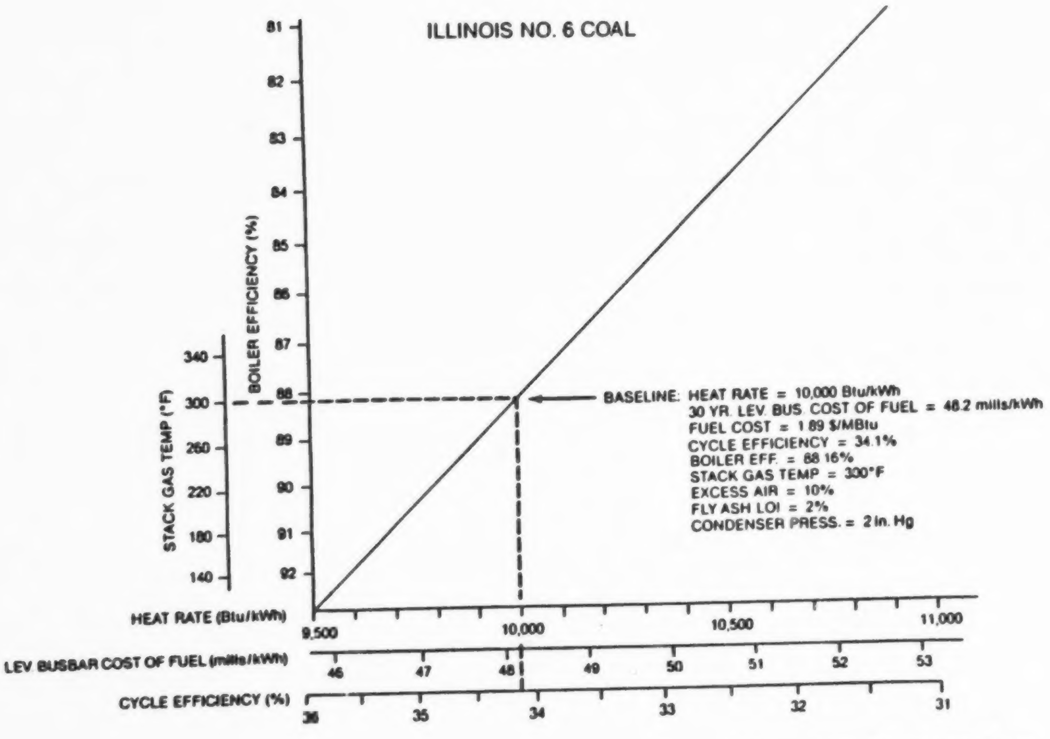


Figure 9. Effect of Lowering Stack Gas Temperature



Reference: *Steam*, Babcock & Wilcox, 1972

Figure 10. Impact of Plant Operating Conditions on Heat Rate

BOILER DESIGN CRITERIA FOR DRY SORBENT SO_X CONTROL WITH LOW-NO_X BURNERS

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ABSTRACT

A program to develop boiler design criteria for application of dry sorbent SO_x control technology with low-NO_x burners is being conducted with EPA sponsorship. A comprehensive review of past and current research in the area of sorbent SO_x control was performed to provide a basis for evaluating the implications of this technology on boiler design, cost effectiveness, and operability. Historical and projected design trends were analyzed for all tangentially fired pulverized-coal utility boilers built during the period 1960 to the present, including the effect of coal rank. The design changes necessary to incorporate dry sorbent SO_x control for utility pulverized coal-fired boilers were evaluated. Among the design and operating factors considered were coal and sorbent type, sorbent-to-sulfur molar ratio, time/temperature history, and back-end effects. Limestone preparation requirements were defined.

INTRODUCTION

Increasing concern for the environmental effects of acid rain has led to a reexamination of the fossil fuel burning electric utility industry. Previously, only new plants were mandated to install pollution control equipment for gaseous emissions under federal New Source Performance Standards (NSPS), although some existing plants were retrofitted with equipment due to local requirements. However, new legislation in response to the acid rain question may require at least a portion of existing oil and coal burning plants to limit emissions of sulfur dioxide (SO_2).

Due to the possibility of regulation of existing plants, various alternative sulfur oxide (SO_x) removal processes are being examined in addition to the tail-end lime or limestone systems predominantly employed to meet NSPS. Because of the combined requirements of "retrofitability", economics, and moderate sulfur removal efficiency, the concept of furnace limestone injection has received renewed interest and study. In the early 1960's, furnace injection originated as a method for controlling SO_2 emissions without involving utilities in sophisticated chemical flue gas treatment systems. However, trials in small-scale furnaces and full-scale utility boilers generally failed to demonstrate sufficient in-furnace SO_2 removal at reasonable sorbent-to-sulfur ratios.

In retrospect, it appears that the high temperatures and oxidizing conditions typical of conventional utility boilers created conditions unfavorable for SO_2 absorption. The development of advanced low NO_x utility boiler combustion technologies may provide new combustion conditions and lower furnace gas temperatures which may be more suited for in-furnace absorption of SO_2 by limestone or other sorbents. The combination of these two technologies has been given the acronym LIMB, representing Limestone Injection with Multistage Burners for NO_x control.

As part of its overall program to evaluate various pollution control technologies, the Environmental Protection Agency, together with Combustion Engineering, Inc. (C-E), initiated a study to assess the impact of dry sorbent furnace injection for controlling sulfur emissions on boiler design and economics. This study comprised a review of sorbent injection data generated to date, past and future boiler design trends, and determination of possible design changes due to the dry sorbent injection and its economics. The preliminary results of this study are presented herein.

HISTORY OF DEVELOPMENT

Removal of SO_x from boiler stack gases by direct, dry injection of alkaline earth compounds into the furnace chamber has been discussed and tested for the past 30 years. During the 1950's, C-E, Ref. (1), developed a process for furnace injection of MgO for control of molten phase vanadium-related high temperature oil ash corrosion and SO_3-related cold end corrosion and acid smuts fallout. Injection of both MgO and dolomite was by means of air aspirators in the furnace cavity and through sootblowers. The SO_3 emissions were usually controlled below 6 ppm, which prevented low temperature metal wastage and air heater plugging. These techniques had little effect on removal of SO_2, which is emitted at a level about 20 to 100 times greater than SO_3, but did provide background for the large-scale injection of dolomite and limestone.

In 1955, a patent issued to John W. Beckman covered a process that would remove SO_2 and SO_3 from combustion gases at temperatures of at least 350°F through the use of finely divided solid calcium carbonate, Ref. (2). In the early 1960's, considerable development work was performed by Wickert in West Germany, as well as Wahnschaffe and associates of Volkswagenwerk in Wolfsburg, West Germany. At Volkswagenwerk, Ref. (3), a hydrated calcined dolomite was injected into a boiler just downstream of the combustion zone. Considerable success was achieved in the removal of SO_2. No boiler fouling problems were encountered. Only limited SO_2 removal was measured when limestone was used as the reactant. These tests were later discontinued due to the high cost of raw material in the plant area.

During the latter part of the 1960's, further investigations were conducted in Japan, Europe, and the United States. Both pilot and full-scale investigations were conducted by the Central Research Institute of Electric Power Industry in Japan, under the direction of Y. Ishihara, Ref. (2). Limestone performed well in the pilot plant, producing 32% to 40% sulfur removal with a calcium-to-sulfur (Ca/S) molar ratio of 1. In the plant tests, hydrated lime was found to perform better than limestone.

In Essen, West Germany, Bergbau-Forschung GmbH, Ref. (4), constructed a 23-foot by 4-inch burner tube to study limestone and dolomite injection. At temperatures up to 1650°F, 80% to 90% SO_2 removal was obtained at a Ca/S molar ratio of 3.

In the United States, bench-scale research was conducted by Battelle Memorial Institute, Ref. (5), under contract to the National Air Pollution Control Administration (NAPCA, an EPA predecessor). In this study, primary emphasis was on additive properties and their behavior under various time/temperature conditions, with respect to both calcination and SO_2 absorption capabilities.

Under sponsorship of NAPCA, and later the Environmental Protection Agency (EPA), R. H. Borgwardt and associates, Ref. (6,7), conducted bench-scale tests on the reaction kinetics of various limestones and dolomites during the late 1960's and early 1970's.

In larger scale tests during this time period, Wisconsin Electric Power Company in 1964 initiated studies of direct injection at their Port Washington, Wisconsin, plant. Dolomitic limestone was mixed and fed with the coal. Most tests were conducted at about 130% of the stoichiometric calcium-to-sulfur molar ratio. Removal averaged 50% at this feed rate for coal with 2.8% sulfur. Deposits which could not be removed by sootblowing were formed on the superheater tubes.

Also on a commercial scale in 1966, C-E, Ref. (8), in conjunction with Detroit Edison, conducted field tests on the injection of both dolomite and limestone into one furnace of a 325 MWe twin furnace unit, followed by wet scrubbing. While introducing sufficient additive to react with all the sulfur in a 2.5% to 3.5% sulfur coal, in-furnace removal efficiencies of about 25% were obtained. No adverse effects on furnace operation were recorded.

Following the C-E tests, the Tennessee Valley Authority (TVA), under contract to the U.S. EPA, conducted limestone injection tests on a 150 MWe pulverized coal-fired boiler at TVA's Shawnee Steam Plant, Ref. (9). In contrast to the earlier bench-scale results and the preliminary findings at Detroit Edison, overall SO_2 removal performance was poor and furnace fouling was significant.

Further work conducted by C-E at Kansas City Power and Light, Ref. (10), Kansas Power and Light, Ref. (11,12), and Union Electric, Ref. (12,13), with furnace injection followed by wet scrubbing, was more in line with the TVA results. Although furnace fouling was not a problem in either case, being dependent on coal ash properties and boiler design, additive reactivity was a problem at both locations and appeared to be reduced by "deadburning" of the additive, caused by calcination at excessive temperatures. Furnace injection was subsequently abandoned at both power plants.

In 1970, Babcock and Wilcox, Ref. (14), issued a research report covering extensive pilot plant work done under NAPCA funding. In the pilot study, a total of 415 tests were conducted with 129 different additives and 7 pulverized coals. Up to 60% removal was obtained at Ca/S molar ratios ranging up to 4. Many process variables were investigated. Based on the behavior of the ash-additive particulate in these tests, it was predicted that furnace fouling would not be a problem. However, resistivity measurements of the particulate matter emitted indicated that electrostatic precipitation performance could be adversely affected.

During the remainder of the 1970's, interest in direct additive injection subsided and was replaced by development of other flue gas desulfurization techniques. However, investigations have again begun, initiated by changes in boiler operating conditions which have the effect of lowering combustion zone temperatures. The changes are due to the high moisture content of low rank coal currently being used and the fact that recently designed boilers are larger to accomplish the same heat transfer. This combination of lower combustion temperatures and increased residence time of the combustion gases in the boiler has proven to be beneficial for SO_2 removal by direct additive injection. Hein and associates, Ref. (15,16), at the Rheinisch Westfaelisches Elektrizitaetswerk, Essen, West Germany, have reported test results from additive injection in a 60 MWe boiler. At a Ca/S molar ratio of 2, better than 75% SO_2 removal was accomplished, and no boiler slagging or fouling problems were reported.

Because of regulations limiting the NO_x emissions, work was also performed in recent years to develop combustion techniques for reducing the formation of NO_x. The techniques involve controlling the amount and location of primary and secondary combustion air and have the overall effect of reducing peak flame temperatures. While operating these burner systems, investigators found that the reduced flame temperature and fuel-rich combustion conditions improve SO_2 removal by direct additive injection.

In tests conducted by Energy and Environmental Research for the EPA, Ref. (17), results from low-NO_x burner facilities have demonstrated the importance of the time/temperature history experienced by the sorbent. Sulfur capture was affected by design parameters, sorbent injection location, and thermal environment and was facility dependent.

Mitsubishi Heavy Industries (MHI), Ref. (18), under contract to the Electric Power Research Institute (EPRI), recently completed a study of limestone furnace injection using a low-NO_x burner. In preliminary reactor tube tests, it was concluded that hydrogen sulfide (H_2S) absorption from fuel-rich conditions was not as effective as SO_2 absorption from a gas containing excess oxygen (O_2). In the 4-ton/hour test furnace, 30% to 40% SO_2 removal was obtained with high sulfur coal (3.3%) and low sulfur coal (0.75%) using limestone at a Ca/S molar ratio of 2 under low-NO_x firing conditions.

C-E, Ref. (19), recently completed a 4 x 10^6 Btu/hr pilot scale test for EPRI in which furnace slagging and fouling behavior with limestone injection during low-NO_x firing conditions was investigated. Two coals were evaluated. For the case of a high sulfur Eastern coal, slagging behavior and deposit friability improved with limestone addition, although deposit buildup was at a faster rate. Slagging and fouling deposit characteristics also benefited from limestone addition for a high sodium Western subbituminous coal. In both cases, SO_2 removal efficiency was dependent on particle residence time at favorable temperatures.

In recent tests reported by Radian Corporation, Ref. (20), limestone was injected into a 52 MWe tangential-firing lignite boiler at Hoot Lake Station of Otter Tail Power Company. Most tests were conducted in a low-NO_x firing mode. SO_2 removal ranged from 20% to 50% at Ca/S molar ratios of from 1.6 to 5. Boiler fouling behavior was also improved.

PROCESS DESIGN CRITERIA

The most important factors which must be considered in evaluating dry sorbent injection as an SO_2 control alternative are coal type and characteristics, sorbent type and characteristics, and its effect on boiler performance.

Coal Type and Characteristics

There are five basic types of coal which are presently being used in the United States and which will continue to be used for at least the next 25 years. These coals are Eastern and Midwestern bituminous (low and high sulfur), subbituminous, Texas lignite, and Northern Plains lignite (low sulfur). Typical analyses for these coals are shown in Table 1. Dry sorbent injection will impact each of these coals differently, generally as a function of sulfur content and coal ash properties.

Coal contains a sizeable percentage of noncombustible ash material, the amount varying with the coal grade. When fired, this material can accumulate on the boiler tubes and, if uncontrolled, can reduce heat transfer and consequently, boiler efficiency. The ash properties are important in determining the performance, slagging, and fouling tendencies of a particular coal. The most important properties are generally considered to be:

Ash fusibility temperature
Base/acid ratio
Silica/alumina ratio
Iron/calcium ratio
Active alkali content
Sodium content
Gravity fractionation

Slagging is the deposition of molten or partially fused ash particles on tube surfaces. The particles are carried by the gas to the furnace walls as well as up to the radiant surfaces in the upper furnace. When the particles strike a cool tube surface, they chill and solidify. Radiant surfaces in the furnace are most susceptible to slagging, but convective surfaces can also slag if gas temperatures exceed prudent levels. Normally, coals with low ash fusion temperatures have a high potential for slagging.

Fouling results from the condensation of the volatile coal ash constituents which have been vaporized during combustion (e.g., sodium sulfate) onto flyash particles and boiler tubes in areas where temperatures are below the dew points of the constituents.

Sorbent Type and Characteristics

Several of the sorbent properties which influence the effectiveness of SO_2 capture and utilization of the sorbent are sorbent type (e.g., lime, limestone, sodium carbonate), calcination reactions (if applicable), particle size, porosity, and time/temperature history experienced by the sorbent. The additive also influences overall SO_2 capture according to the calcium-to-sulfur molar ratio employed and the quality of dispersal of the additive in the flue gas.

Additives used for furnace injection normally are calcium, magnesium, or sodium alkalis. By far the most common alkali employed has been calcium-based, and of these compounds, calcium carbonate has been most extensively used. As a result, most of the information presented concerning sorbents deals with calcium carbonate (limestone), with other compounds discussed where information is available.

The general term "limestone" covers a broad range of materials varying in calcium and magnesium content--from calcite or argonite ($CaCO_3$) to dolomite ($MgCO_3.CaCO_3$). The terms "high-calcium limestone" (very low in magnesium carbonate ($MgCO_3$)) and "dolomite limestone" (approaching dolomite in $MgCO_3$ content) are commonly employed. $MgCO_3$ content affects SO_2 absorption because it does not behave like $CaCO_3$, in regard to either calcination or reaction with SO_2.

Limestones vary widely in their chemical composition and crystal structure, with the result that material from one source may differ from another in degree of porosity developed during calcination and, therefore, in absorption efficiency.

For the three compound types mentioned--calcium, magnesium, and sodium--the calcination reactions are as follows:

$$CaCO_3 \xrightarrow{\text{Heat}} CaO + CO_2$$

$$MgCO_3 \xrightarrow{\text{Heat}} MgO + CO_2$$

$$Na_2CO_3 \xrightarrow{\text{Heat}} Na_2O + CO_2$$

In an early fundamental study by Battelle, Ref. (5), the equilibrium dissociation pressure of carbon dioxide (CO_2) maintained by limestone was plotted as a function of temperature. These data, shown in Figure 1, demonstrate that a temperature of about 1400°F is necessary to keep the calcined limestone from recombining with CO_2 at a typical furnace CO_2 concentration of 14.5%.

In addition to the kinetics of additive calcination, temperature and residence time play a major role in determining final particle size, porosity, and, therefore, total available surface area. Based on reports of Battelle and Borgwardt, Ref. (6,7), the most important factors in determining the reactivity of a given limestone are the surface area and porosity developed during calcination. These factors directly determine the availability of lime for reaction, the accessibility of the lime, and the space which is available within a given particle for reaction products. The surface area and porosity are determined by calcination rate and sintering rate. The latter is more important in determining the decreased reactivity of limestones at high temperatures. Sintering itself is a complex process, depending on grain size, impurity content, lime temperature, and calcination time.

Testing by MHI in a 1-inch diameter tube reactor demonstrates the significant effect of residence time on SO_2 removal. As shown in Figure 2, Ref. (18), SO_2 capture increased dramatically with increasing residence time.

Additive calcination and reactivity as related to particle size and porosity is a complex phenomenon. Most investigators have observed a leveling off in performance as particle size is decreased. This may be due to the interaction of pore diameter and particle diameter. For larger particles, pore diameter may be important, while for smaller particles, the effect is minimized. Another factor which may limit the effectiveness of smaller particles is mass transfer. The fine particles should have less slippage in the gas stream than larger ones, and less relative motion between solid and gas.

Selecting the appropriate sorbent/sulfur ratio can have a significant effect on the economic viability of LIMB for a particular unit. Tests have shown that high- and low-sulfur coals can require significantly different amounts of sorbent per mole of sulfur. The selected ratio determines the impact on all other components and subsystems, including gas cleanup, limestone preparation, and the boiler itself.

For this study, a Ca/S molar ratio of 2 was used for high-sulfur coals, and a Ca/S molar ratio of 4 was used for low-sulfur coals. These ratios were selected after considering several trade-offs between incremental SO_2 removal and the penalties associated with increased sorbent requirements. For low-sulfur coals, tests have shown that little additional SO_2 removal is achieved at Ca/S molar ratios above 4. The added requirements for pulverizing and transporting additional sorbent, plus the increased back end requirements, more than offset the benefits of added SO_2 removal. For high-sulfur coals, the major consideration is solids carryover. At a Ca/S molar ratio of 2, for a 3% sulfur coal, the solids loading would be 150% greater than without sorbent injection (compare with 50% greater loading for a 0.5% sulfur coal at a Ca/S molar ratio of 4). This solids loading increase will have an adverse effect on ESP performance. Increased sootblowing will be required to remove the (anticipated) increased deposits in the convective sections.

Sorbent Preparation

Sorbent handling and storage can be carried out with essentially the same equipment conventionally utilized for coal. Commercially available components have been combined in the various demonstration systems, all of which have operated successfully.

Pulverizers are designed to provide a selected particle size when grinding materials of a similar hardness and density. Because limestone, for example, is denser than most coals, simultaneous pulverization of limestone and coal would result in excessive mill rejects if adequate control on limestone particle size was maintained. Therefore, a limestone preparation system would be designed to include separate mills dedicated to limestone pulverization alone.

From the mills, the sorbent is sent to storage silos, from which it is transported via dense- or dilute-phase transport pumps to the boiler. A dense-phase system delivers about 20 lb solid/lb air. The advantage of this system is the small amount of air required to transport the sorbent. The major disadvantages are the high pressure loss (roughly 40 to 60 psig) and associated sealing problems. A dilute-phase system requires about 1.5 lb air to deliver 1 lb of sorbent. The pressure drop is in the range of 10 to 20 in w.g. The split between primary air, overfire air, and sorbent transport air will have to be carefully controlled to maximize combustion and SO_2 removal efficiencies.

Figure 3 shows a typical limestone preparation and injection system.

Sorbent Injection Considerations

Many different schemes have been tried for injecting sorbent into boilers for sulfur removal. From these tests, several criteria for injecting sorbent to achieve the most beneficial results have been determined: (1) maximize sorbent particle residence time in the "critical" temperature region (between 1400°F and 2200°F, where the calcium/sulfur reaction to form calcium sulfate is most favorable); (2) minimize the time the sorbent particle is subject to hard burning (above 2700°F); (3) maximize the particle surface area; and (4) maximize the mixing between sorbent and flue gas.

Because of the short retention time in most utility boilers, it is important for the sorbent to be distributed rapidly over the boiler cross section in order to contact all areas of the gas stream. If time is lost in achieving the proper distribution, then some portions of the stream will not have enough time for good absorption after the sorbent becomes available.

Distribution is a difficult problem because of the very large cross section of modern boilers, the rapid flow of the gas, and the small size of the particles. In most injection systems, the particles are carried in a body of injection gas, so that the problem becomes one of fluid dynamics--the mixing of one body of gas with another.

In addition to mixing considerations, the location of sorbent injection also determines the temperature encountered, gas mixture (reducing or oxidizing) and particle residence time. These factors can influence both calcination of the additive and the reactions between sulfur species in the gas phase and the additive.

MHI has carried out a comprehensive series of tests at their 4-ton/hr pilot plant during which they evaluated four methods of introducing the sorbent into the furnace as shown in Figure 4: (A) with the coal, premixed; (B) through auxiliary air nozzles; (C) through overfire air nozzles; and (D) through gas recirculation nozzles, Ref. (18). The best performance was achieved by introducing the sorbent through the overfire air nozzles, with 57% SO_2 removal at a Ca/S molar ratio of 3.

Steam Generator Efficiency

Sorbent injection introduces several additional losses which adversely affect the overall steam generator efficiency. These are:

1. Heat required for calcination
2. Increased dry gas loss
3. Increased flyash heat loss
4. Increased ash pit loss

The magnitude of the efficiency reduction depends on the sulfur content of the coal and the calcium-to-sulfur molar ratio. For high-sulfur coals, these losses will be offset to a degree by an efficiency gain resulting from a decrease in the allowable gas temperature leaving the steam generator envelope. This relates to the fact that boiler efficiency is very sensitive to the gas exit temperature, which is largely dictated by the coal sulfur content. Typically, this temperature is about 155°F for coals containing up to 1% sulfur and 180°F for coals containing 3% to 5% sulfur. A reduction in the concentration of SO_2/SO_3 at the boiler exit will reduce the potential for cold-end corrosion and permit a lowering of the exit gas temperature.

Effect of Sorbent Injection on Overall Steam Generator and Component Performance

Sorbent injection greatly increases the quantity and changes the character of the solids passing through a steam generator. As a consequence, because the slagging and fouling characteristics are changed, the overall steam generator efficiency and the performance of the individual components (e.g., superheater and reheater outlet temperatures) are affected.

It is expected that a low-NO_x firing system plus sorbent injection will result in an improvement in waterwall deposit friability (ease of removal) and sootblower effectiveness for most coals. For retrofit units firing coals which exhibit severe slagging in the presence of sorbent, the steam generator capacity may be adversely affected. If slagging is excessive, it may inhibit waterwall absorption, reducing evaporation and raising the furnace outlet gas temperature (FOT, defined as the temperature at the bottom of the vertical radiant surfaces (panels) suspended in the upper section of the furnace). If increased sootblowing frequency is not adequate to alleviate this problem, the unit capacity may have to be reduced. For new units, these potential waterwall slagging problems may be minimized by including larger furnaces in the design.

Superheater and reheater outlet temperatures are determined by FOT, gas flow, and the degree of fouling on the heat transfer surfaces. An FOT which is higher than the design value results in higher superheater and reheater temperatures. These temperatures are normally controlled by manipulating burner tilts, excess air, and superheater/reheater spray. However, since the latter two options have considerable influence upon the overall plant efficiency, their use should be minimized. As in the lower furnace section, the increase in solids loading with sorbent injection will result in an increase in the deposit rate on superheater and reheater surfaces. This will require an increase in the sootblowing frequency. For new units, design considerations may include the use of wider spacing in the convective section to prevent tube bridging from deposit buildup and/or the addition of widely spaced superheater panels to reduce the gas temperature before the gas enters the convective sections.

Sorbent injection will result in an increase in the gas/solids mass flow through the steam generator. In retrofit applications, this will result in an increase in the mass velocity through the unit. While this increased velocity will cause an increase in the convective heat transfer coefficient, it is important to keep the velocity within acceptable limits to minimize tube erosion. The maximum allowable gas velocity depends on the erosion characteristics of the flyash and the quantity of flyash. For conventional coal-fired units, the general practice is to limit the maximum velocity to approximately 50 to 70 feet per second. With sorbent injection, this velocity may have to be reduced, due to the increased solids loading and the ash erosion characteristics (not yet known). In a retrofit application, widening the spacing between tube elements to lower gas velocity may not be economical. A reduction in unit capacity may, therefore, be required to keep the gas velocity within acceptable limits. For new units, the convective section can be designed with wider transverse spacing to keep the gas velocity below the maximum value.

The final heat transfer sections located within the steam generator envelope are the economizer and the air preheater. Prior to the early 1970's, most economizers were of a finned-tube staggered arrangement design. The significant increase in solids loading with sorbent injection would make this type of economizer very susceptible to plugging. Therefore, for retrofit units which incorporate finned economizers, it may be necessary to replace the economizer with one featuring bare tubes with an in-line arrangement. This will generally result in a larger economizer to accomplish the same amount of heat transfer. In some cases, installation of a larger economizer may be impractical due to space limitations. Insufficient economizer surface results in a reduction in the quantity of steam evaporated in the steam generator. For some coals, this may be fully or partially overcome by tilting the coal nozzles downward and/or increasing the frequency of sootblowing in the furnace to remove accumulated deposits and increase waterwall absorption.

Studies performed on air heaters during limestone or dolomite injection have shown that, with reduced SO_3 levels in the gas stream, plugging, as indicated by pressure drop across the air heater, is reduced to a minimum. While the ash loading is increased, the actual buildup decreases, and that which forms tends to be fluffy and readily removable. Low temperature probe studies conducted during full scale limestone furnace injection tests showed that SO_3 was reduced to a level sufficiently low to eliminate corrosion and produce deposits which are dry and generally non-adherent.

For units which will require increased sootblowing frequency and/or sootblower coverage, it may be necessary to upgrade the capacity of the sootblowing system. It should be noted, however, that the additional steam or air consumption required to accomplish this will have an adverse impact upon steam generator and overall plant efficiency.

The increased gas flow rate through the convective sections which is associated with sorbent injection will result in higher draft losses for retrofit units. These facts must be considered in evaluating the capacity of an induced draft fan.

Solids Removal

Sorbent injection dramatically increases the particulate loading leaving the boiler. This quantitative change is coupled with changes in the chemical and physical properties of the solid material. These changes impact the performance of existing back end equipment in retrofit situations and dictates the selection of equipment for new units.

There is relatively little information available on the effect of sorbent injection on ESP performance, although there is ongoing work in this area by the EPA. For retrofit applications, some improvement in ESP performance can be realized by SO_3 conditioning. Tests have shown that LIMB flyash resistivity can be significantly reduced by injecting small amounts of SO_3 ($\sim$5 ppm), increasing the flue gas moisture content, and/or decreasing the outlet temperature to less than 250°F. Additional research is needed in this area before the extent of ESP modification can be defined.

Units equipped with wet scrubber systems are not viable candidates for LIMB retrofitting. Besides providing little added SO_2 reduction, the reactive alkaline oxides could create scaling problems under certain conditions.

The concept of dry scrubbing is a preferred method for tail-end SO_2 removal in certain situations. This technique offers the potential of a "combined system" - furnace injection followed by dry scrubbing. Calcined sorbent could be recycled from the spray dryer bottom or particulate collection device into the spray dryer. It has been demonstrated that this collected sorbent can be successfully used as a spray dryer feed stock, albeit with reduced effectiveness.

With sorbent injection into the furnace, all ash hoppers will experience a higher loading. In general, ash hoppers are oversized to accommodate a range of ash loadings from various coals. It is reasonable to assume that no modifications will be required to compensate for additional ash. Approximately 20% to 30% of the total solids are expected to be collected in the hoppers. The operational frequency of the ash removal systems will have to be increased with the higher solids loadings.

HISTORICAL AND PROJECTED DESIGN TRENDS

A survey of key design parameters for C-E coal-fired boilers was undertaken to provide guidelines for establishing criteria for site selection and for identifying those parameters which are influential in designing for dry sorbent injection. The survey covered a total of 273 units sold from 1960 to 1982. Of this total, 179 coal-only units sold between 1960 and 1980 to domestic utilities were defined as the basis for study.

Among the parameters considered were unit size, coal rank and emission control capabilities. These data are presented in Tables 1 and 2 and Figures 5 and 6.

As discussed earlier, there are five basic types or ranks of coal which have been used during the last 25 years. As can be seen in Table 1, there is a wide variation in heating value as well as moisture, ash, and sulfur content. The ash analyses vary considerably . These differences significantly influence boiler design and operation. Figure 5 shows the selected sample of boilers segregated by primary coal fired and contract year. Note the shift from Eastern bituminous to subbituminous and lignite coals. The factors most directly responsible for effecting this shift in coal fired were the advent of more stringent federal emission regulations in 1970 and industrial expansion of the Western and Southern United States. The low sulfur content of the subbituminous and lignite coals makes them more attractive from a capital outlay standpoint, since this greatly reduces the amount which must be spent on expensive cleanup equipment. Figure 6 shows the breakdown by fuel type as a percentage of total sample generating capacity.

Table 2 shows the emission control capabilities of the sample units. Over 90% of the units incorporate some form of particulate control device, with the electrostatic precipitator the overwhelming choice. Over half of the units are equipped with overfire air capability for NO_x control. This method for controlling NO_x, which lowers the flame temperature by burning the fuel in two stages, has proven to be both successful and economical on units equipped with tangential burners. Only about 29% of the sample units are equipped with flue gas desulfurization capability. As can be seen from Table 2, there are many processes available for removing SO_2 from flue gas, with limestone scrubbing being the most frequently selected method in this sample. Of 52 units incorporating some type of FGD, only two were ordered before 1970.

GENERIC PROCESS DESIGN AND ECONOMICS

From the sample of C-E coal-fired units described above, three candidate retrofit units were selected in the 200 MWe, 400 MWe, and 600 MWe size ranges. All three units burn high sulfur Midwestern bituminous coal, are equipped with ESP's and do not presently have FGD capability. At present, work is in process to define the boiler modifications and additional equipment required to retrofit these units for dry injection SO_x control. In addition, six new units in the same size ranges (three high sulfur coal, three low sulfur coal) are being evaluated to determine the added costs of incorporating dry sorbent SO_x control.

Following the completion of the generic process design for these new and retrofit units, detailed cost analyses will be carried out to determine the economic viability of LIMB as a SO_x control option. The results of these economic analyses will be reported at a later date.

ACKNOWLEDGEMENTS

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TABLE 1

Typical Coal Analyses

	Eastern Bituminous	Midwest Bituminous	Sub-bituminous C	Texas Lignite	Northern Plains Lignite
Total Moisture, %	5.0	15.4	30.0	31.0	39.6
Ash, %	10.3	15.0	5.8	10.4	6.3
Volatile Matter, %	31.6	33.1	32.6	31.7	27.5
Fixed Carbon, %	53.1	36.5	31.6	26.9	26.6
Total %	100.0	100.0	100.0	100.0	100.0
Btu/lb, as Fired	13,240	10,500	8,125	7,590	6,523
Btu/lb, Moisture & Ash Free	15,640	15,100	12,650	12,940	12,050
Fusion Temperature (reducing), °F					
Initial Deformation (ID)	2,170	1,990	2,200	2,075	2,027
Softening (ST)	2,250	2,120	2,250	2,200	2,089
Fluid (FT)	2,440	2,290	2,290	2,310	2,203
Ash Analysis, %					
SiO_2	40.0	46.4	29.5	46.1	23.11
Al_2O_3	24.0	16.2	16.0	15.2	11.29
Fe_2O_3	16.8	20.0	4.1	3.7	8.48
CaO	5.8	7.1	26.5	16.6	23.75
MgO	2.0	0.8	4.2	3.2	5.87
Na_2O	0.8	0.7	1.4	0.4	7.38
K_2O	2.4	1.5	0.5	0.6	0.70
TiO_2	1.3	1.0	1.3	1.2	0.45
P_2O_5	0.1	0.1	1.1	0.1	-
SO_3	5.3	6.0	14.8	12.7	17.69
Not Accounted For	1.5	0.2	0.6	0.2	1.28
Sulfur, %	1.8	3.2	0.34	0.6	0.75
Lb Moisture/10^6 Btu	3.8	14.7	36.9	40.8	60.7
Lb Ash/10^6 Btu	7.8	14.3	7.1	13.7	9.7
Lb Sulfur/10^6 Btu	1.36	3.05	0.42	0.79	1.15
Base/acid Ratio	0.426	0.473	0.784	0.392	1.33
Hardgrove Grindability	55	56	43	48	25*

(*) With 39.6% moisture at pulverizer inlet, range is 20-50.

TABLE 2

Number of Units Installed with Air Quality Control Systems

		NO. OF UNITS	% OF TOTAL
Particulate Control			
Electrostatic Precipitator		146	
Wet Scrubber		7	
Fabric Filter		12	
Mechanical Cyclone Collector		1	
	Total	166	93
Fuel Gas Desulfurization			
Limestone		22	
Lime		11	
Lime/Limestone		4	
Lime/Alkali Flyash		9	
Double Alkali		1	
Sodium Carbonate		1	
Lime/Spray Drying		4	
	Total	52	29
NO_x Control			
Overfire Air		91	
	Total	91	51

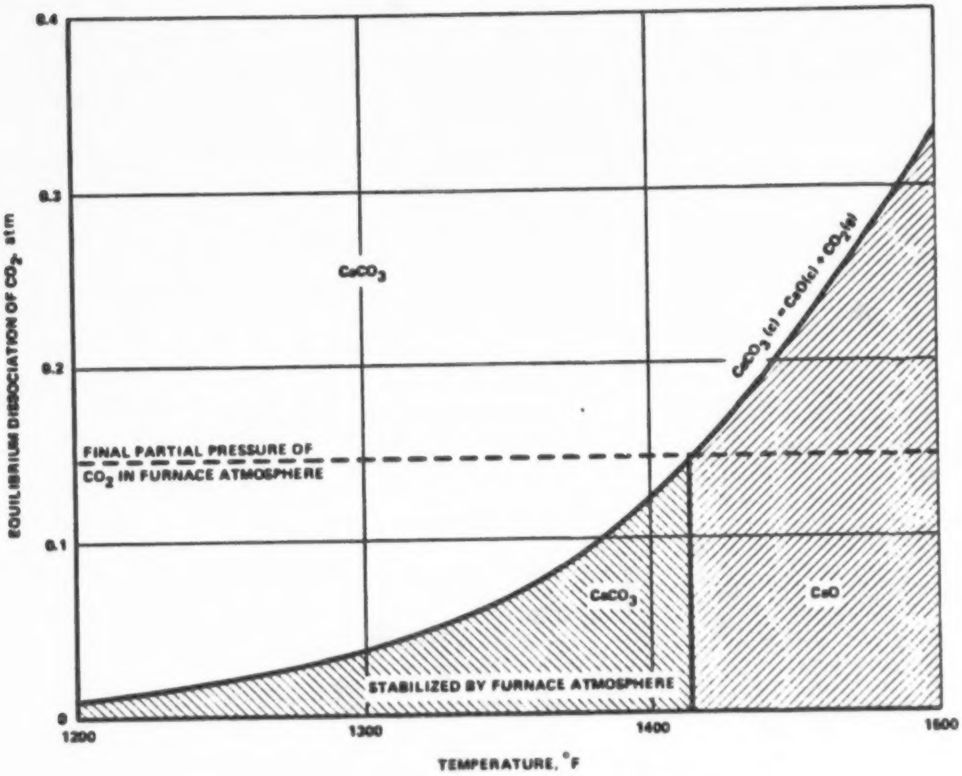

Figure 1 Effect of furnace atmosphere on dissociation of $CaCO_3$ (Ref. 5).

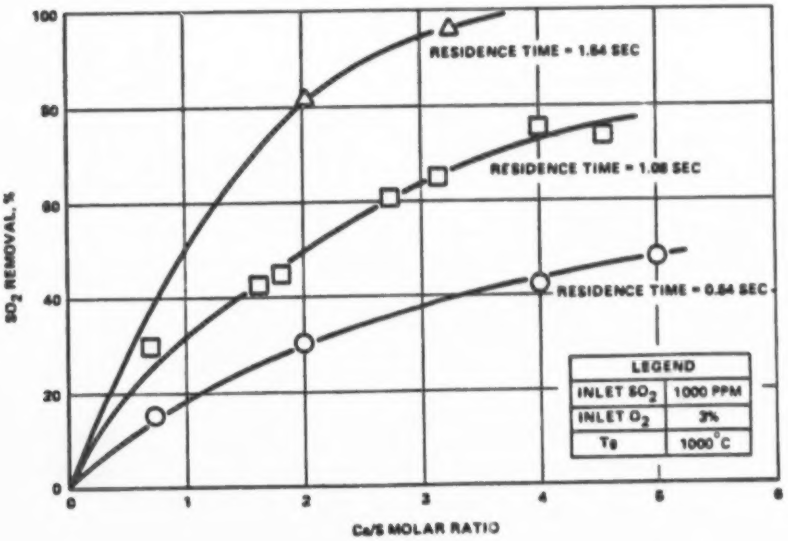

Figure 2 Relation between SO_2 removal and Ca/S molar ratio (Ref. 18).

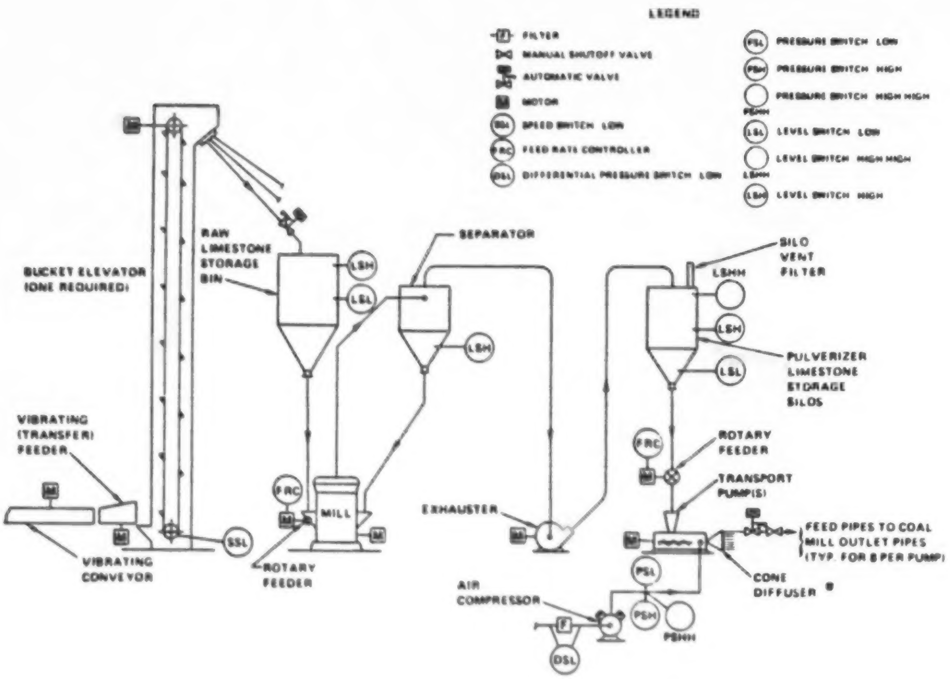
LEGEND
F FILTER
MANUAL SHUTOFF VALVE
AUTOMATIC VALVE
M MOTOR
SSL SPEED SWITCH LOW
FRC FEED RATE CONTROLLER
DSL DIFFERENTIAL PRESSURE SWITCH LOW
PSL PRESSURE SWITCH LOW
PSH PRESSURE SWITCH HIGH
PSHH PRESSURE SWITCH HIGH HIGH
LSL LEVEL SWITCH LOW
LSHH LEVEL SWITCH HIGH HIGH
LSH LEVEL SWITCH HIGH
BUCKET ELEVATOR (ONE REQUIRED)
RAW LIMESTONE STORAGE BIN
SEPARATOR
SILO VENT FILTER
PULVERIZER LIMESTONE STORAGE SILOS
ROTARY FEEDER
TRANSPORT PUMP(S)
FEED PIPES TO COAL MILL OUTLET PIPES (TYP. FOR 8 PER PUMP)
CONE DIFFUSER
VIBRATING (TRANSFER) FEEDER
VIBRATING CONVEYOR
MILL
ROTARY FEEDER
EXHAUSTER
AIR COMPRESSOR

Figure 3 Limestone preparation and injection system (Ref. 21).

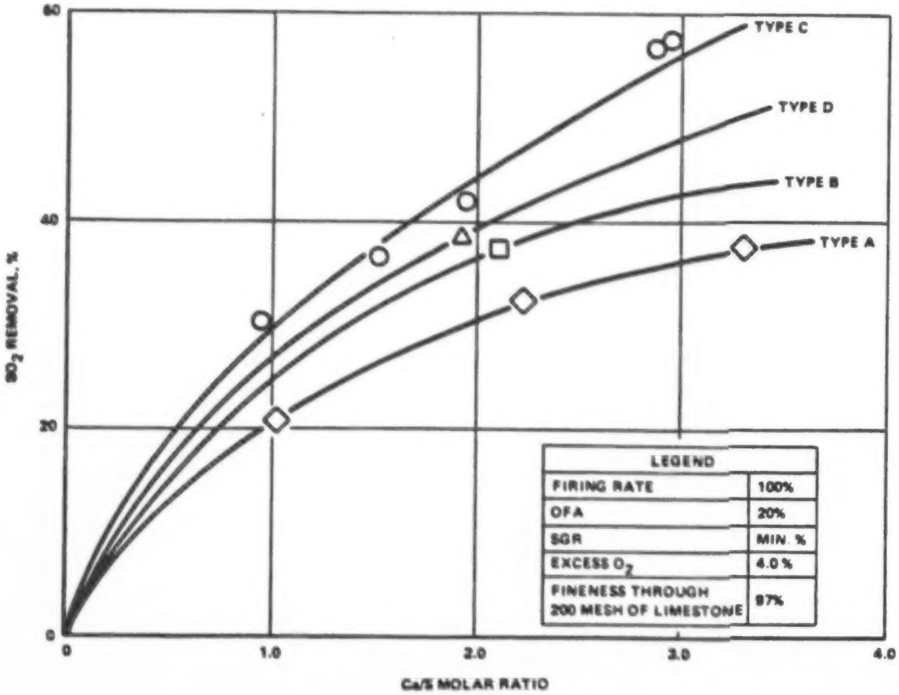

Figure 4 Comparison of SO_2 removal rate with various methods of injection (high-sulfur coal) (Ref. 18).

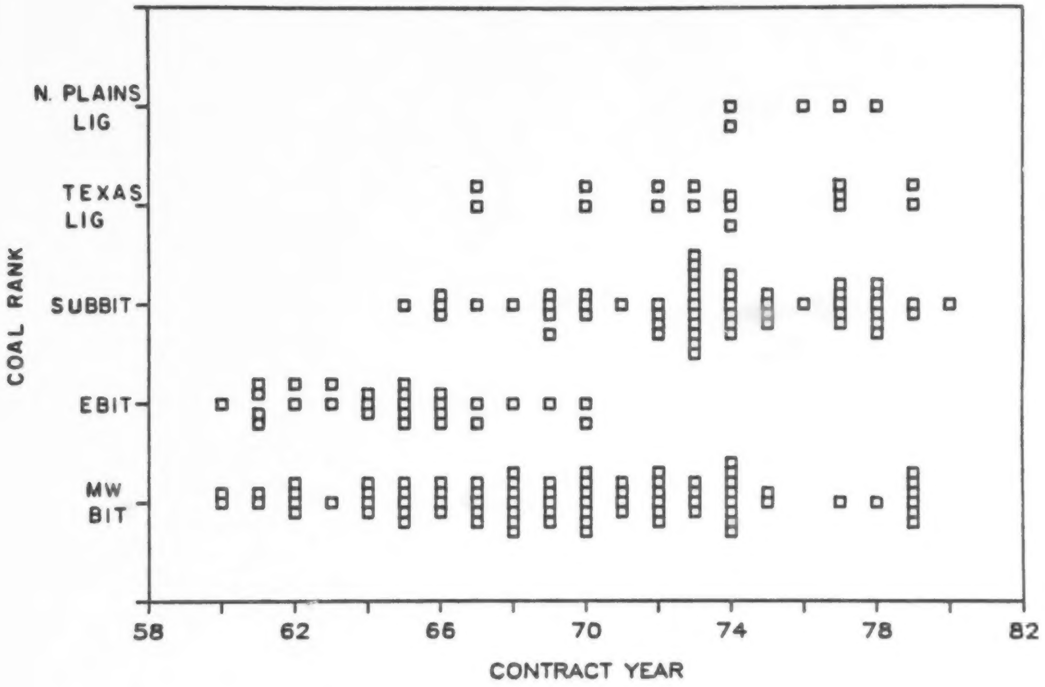

Figure 5 Coal rank vs. contract year

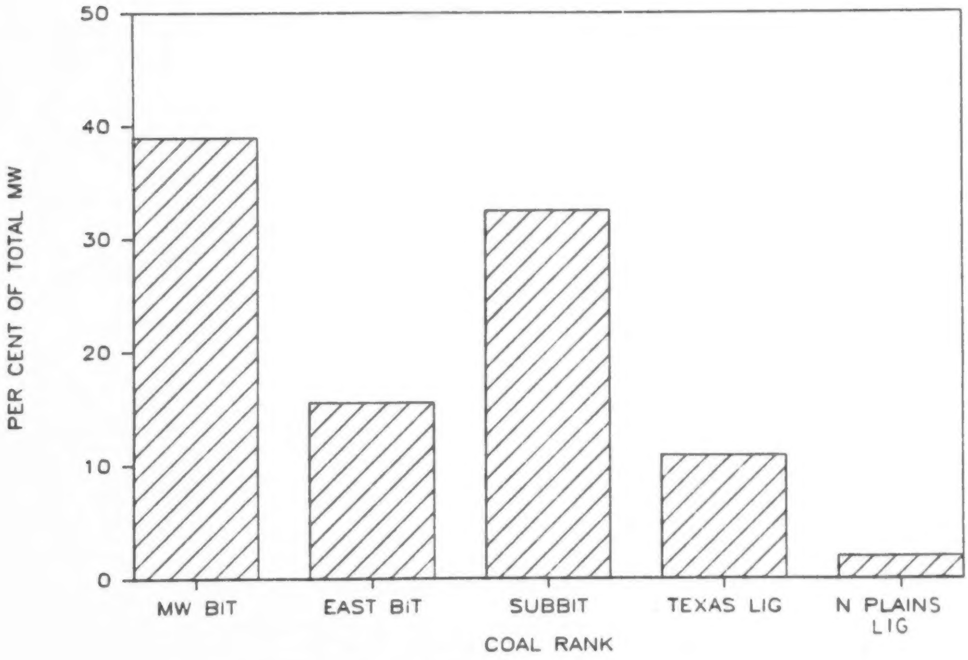

Figure 6 Distribution of total generating capacity by coal rank (Total MW =96,322).

WALL-FIRED BOILER DESIGN CRITERIA FOR DRY SORBENT SO_2 CONTROL WITH LOW-NO_x BURNERS

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ABSTRACT

Limestone injection multistage burner (LIMB) technology is being actively investigated as a potentially economical and attractive means of reducing SO_2 and NO_x emissions in coal-fired boilers. Although primary emphasis is on the retrofit potential for existing boilers that are not currently equipped with scrubbers, application to new boilers is being investigated as well.

This paper concentrates on LIMB technology for new and existing coal-fired power stations and also discusses historical and projected design trends which have an effect on it. Advantages and disadvantages of various LIMB methods are discussed, including the effect on steam generator design criteria. A suggested approach is developed, and its ramifications on the boiler and the balance of plant design are discussed.

INTRODUCTION

Injection of dry sorbents into the furnace area of steam generating units is not a new technology. Many years ago, limestone was injected in an attempt to reduce low temperature corrosion and high temperature fouling in the convection passes of steam generators.[1] While it may have helped, it was expensive and its use was not widespread.

More recently, during the late 1960s and early 1970s, limestone injection was evaluated for removal of SO_2 from the products of combustion.[2,3] Removal efficiencies varied from 15 to 50 percent. However, the majority of cases averaged about 20 percent SO_2 removal. Tests were run on horizontally fired, vertically fired, and tangentially fired units during this period. Limestone was generally introduced into the furnace with the fuel, although injection above the burners was also tried on a wall-fired unit. Some of the problems encountered included "deadburning" of the sorbent (thermal deactivation) along with fouling of the convective passes and loss in electrostatic precipitator removal efficiency. The programs were abandoned but, with the advent of low-NO_x burner technology, were revived around 1979.

Low-NO_x burner technology stages the combustion process, producing lower flame and gas temperatures in the lower portions of the furnace. U.S. Environmental Protection Agency (EPA) pilot scale tests conducted around 1979 indicated the possibility of 70 percent removal of SO_2 with limestone injection through low-NO_x burners at reasonable Ca/S molar ratios. In 1980, the EPA initiated it's limestone injection multistage burners (LIMB) program to identify the process variables that resulted in the high capture observed in the pilot scale studies. The program's objective is to develop LIMB and low-NO_x burner technology for both retrofit and new applications.

BACKGROUND

Riley Stoker Corporation conducted a survey of its pulverized coal-fired utility boilers greater than 100 MWe sold during the last 25 years. Riley has constructed two basic types of wall-fired boilers during this period: one conforms to the wall-fired configuration for the general boiler industry and the other is a unique type designated the Riley TURBO® furnace. These design types are illustrated in Figure 1 for comparison. Wall-fired units can have burners installed on either or both of the front and rear waterwalls and also on one or more levels. In contrast, the Riley TURBO furnace always has burners installed as opposed pairs and at one elevation. The survey was directed at compiling general design and operational parameters, including but not necessarily limited to:

- Boiler population as a function of start-up year and coal rank
- Operating characteristics
- Boiler design trends including furnace geometry and heat releases
- Slagging and fouling characteristics
- Impact of NO_x control

The general trends noted during this survey indicate that the period from 1965 to 1970 contains the units with the least amount of overages or leeways in design. Units were physically smaller and heat release volumes and rates were higher during this period. Also, the majority of units were designed for pressurized operation. The costs of induced draft fans and their associated controls were eliminated on pressurized units. By the mid-1970s, this trend had reversed, and nearly all units designed for coal firing were for balanced draft operation.

Figure 2 shows a plot of unit capacity versus start-up year. The unit capacity is in pounds of steam per hour, and there is a definite trend to increasing steam capacities up to 1970 where it has leveled off. There are a number of reasons for this, including the drop-off in supercritical unit designs and the switch to oil- and gas-fired units for the larger capacities.

Another consideration for the leveling off of the unit capacities is the advent of nuclear power. During the 1970s, nuclear units coming on line would handle the base load capacity requirements of the utilities. This left cycling and peaking type boilers, which were generally smaller in capacity than base loaded central station units, to meet the peak load demands.

Volumetric heat release rate has been plotted in Figure 3 for both Riley designed units and the general boiler population. The volumetric heat release rate is defined as the gross heat input to the furnace divided by the furnace volume (see Figure 4). The volumetric heat release rate is used as an indication of availability of space to complete the combustion process. Both trends are similar and show a gradual increase in heat release rate until approximately 1970 when the value started coming down in magnitude.

The effective projected radiant surface (EPRS) is calculated by creating an imaginary plane through the center line of waterwall and radiant superheater tubes. The flat surface is then calculated considering both sides of the plane on radiant superheater or waterwall platens and the furnace side of the waterwalls proper. The heat release rate on a square foot of effective projected radiant surface, shown in Figure 5, follows the same trend as volumetric heat release. There is a tendency to increase during the 1960s and to taper off during the 1970s. While part of this reduction can be attributed to air pollution requirements, the remainder can be explained by the reductions in coal quality. Lower rank Western sub-bituminous coals are low in both heating value and sulfur content, and more units are being designed for these coals during the 1970s.

Coal rank can affect many parameters in boiler design. During the 1960s and early 1970s, bituminous coal was used for the bulk of units designed for solid fossil fuel firing. During the middle and late 1970s, Western subbituminous and lignite coals permeated the market to the point that they represent approximately 50 percent of the coals used for new designs during that period.

Furnace exit gas temperatures have not changed significantly between the various ranks of coal. As shown in Figure 6, the furnace exit gas temperature range is plotted against the type of coal used in Riley Stoker designs. The predominance of the data is between 1900 and 2000°F. Part of the variance is due to an effort to maintain the furnace exit gas temperature well below the ash softening temperature of the coal. (Riley Stoker does not have any pulverized lignite fired units so lignite is not shown in Figure 6.)

In the early 1970s, government regulations for air quality control forced a turnaround in the size of the furnaces. During that period, one of the first methods of NO_x control was to lower peak temperatures in the flame zone, requiring larger furnaces to cool the combustion process and complete burnout of the fuel. This resulted in a decrease in heat release rates and furnace exit temperatures.

Currently, there is essentially no new fossil fuel utility boiler construction. When the utility industry does pick up, it is expected that the trends that were observed in the late 1970s will continue. Units will be of moderate size due to high interest rates and a slowdown in the growth rate of load demand.

The remainder of this paper discusses the approach to achieving both low-NO_x and low-SO_2 emissions using LIMB technology (see Figure 7). The effect on the boiler and the balance of plant equipment associated with the limestone injection technology is also discussed.

APPROACH

The goal of the ongoing EPA-sponsored LIMB program is to develop in-furnace sorbent injection combined with low-NO_x burner technology leading to industry demonstration and commercialization of LIMB technology in the near term. In consideration of this, specific LIMB objectives include a 50 to 60 percent reduction from uncontrolled levels of both SO_2 and NO_x in retrofit applications. Objectives for new LIMB-equipped plants would include a 70 to 90 percent reduction in SO_2 and a 70 to 80 percent reduction in NO_x in retrofit applications from uncontrolled levels. These objectives are believed to be achievable with LIMB alone in the retrofit case and LIMB in combination with additional sulfur removal technology (if required) for new units.

LIMB appears to be particularly attractive since it is not space, hardware, or maintenance intensive and is therefore retrofittable to many existing plants at a fraction of the cost of scrubbers. Costs are expected to be at least $100/kW less than for scrubbers.[4] LIMB cost predictions to date have varied from ten to fifty percent of scrubber cost.[5,6,7]

Much basic research and pilot scale work has been and continues to be done toward the achievement of these objectives, and a full scale utility demonstration project is scheduled to commence late this year with start-up in late 1986.

Various configurations of LIMB-equipped plants have been conceived to meet the SO_2 and NO_x removal objectives discussed above at a cost significantly less than that of scrubber-equipped plants. Significant variables affecting plant design include:

- Boiler/firing configuration
- Burner design for low NO_x
- Coal type/sulfur content
- Sorbent type/size
- Calcium-to-sulfur molar ratio
- Time/temperature requirement for sorbent/SO_2 reaction
- Sorbent injection method
- Slagging/fouling/erosion potential
- Ash loading and resistivity
- Ash constituents' effect on disposal

Discussion in this paper is directed toward utility size pulverized coal boilers equipped with low-NO_x burners. Effects of various coal sulfur contents are discussed where they are expected to have a significant impact on LIMB design. The sorbent considered is high calcium limestone with calcium-to-sulfur molar ratios ranging from approximately 2 for high sulfur coal to 4 for low sulfur coal, where a higher percent sulfur capture is feasible. Limestone is finely ground and pneumatically introduced in the furnace separate from the coal. Soot blowers are provided as necessary for control of fouling. Existing particulate removal equipment is expected to be maintained on retrofit application. Because of increased ash loading and increased ash resistivity, modifications such as added mechanical collectors, precipitator renovation/expansion, and/or flue gas conditioning will be required on many applications with older precipitators. New units are expected to be equipped with fabric filters. Ash must be handled dry to avoid the cementitious characteristics of the alkaline material when wetted, and ash disposal will be complicated by the increased ash quantity and unknowns relative to LIMB ash disposal requirements.

EFFECT ON BOILER

The heart of the LIMB system is the low-NO_x burners and the sorbent injection system. Low-NO_x burners are generally designed with combustion air added in a staged manner, ensuring a fuel-rich zone early in the combustion process. This chemically reducing zone tends to lower NO_x production from oxidation of the nitrogen in the fuel and combustion air. Figure 8 illustrates a Riley Stoker low-NO_x burner concept and shows how combustion air is added in a staged sequence with the coal. This burner, which incorporates tertiary air ports for staging, was designed according to criteria developed under EPA low-NO_x burner demonstration programs. Although not shown in Figure 8, the coal nozzle incorporates the same venturi discharge section and conical coal spreader as that used in a retrofit low-NO_x burner design called the Controlled Combustion Venturi (CCV) burner.[9]

The CCV burner is shown in Figure 9. The design is very similar to pre-NSPS equipment (single-register flare burner) with the exception of a smaller diameter modified coal nozzle and spreader. The round coal nozzle discharge was modified to include a venturi section while the original multi-vaned coal spreader was replaced with a four-bladed conical shaped spreader. Both the spreader position and the nozzle setback position can be adjusted during operation. These modifications produce the mixing and combustion characteristics necessary for low-NO_x. Figure 10 shows the flame shape produced by the CCV burner as compared to the flame shape typical of the pre-NSPS (flare type) burner. The CCV burners have been retrofitted to existing units, with test results showing a 50 percent reduction in NO_x levels achieved with acceptable unit performance.

New unit designs could incorporate the CCV burner with tertiary air ports installed to get even greater reductions in NO_x levels based on uncontrolled measurements with pre-NSPS burner equipment.

The use of tertiary air ports or overfire air ports with low-NOx burners provides alternate locations for injection of the sorbent. As mentioned previously, initial work with sorbent injection showed low SO_2 capture due to sorbent deactivation. This occurred when the sorbent, which was injected directly with the fuel, reached high temperatures and sintered, forming a hard crust which prevented the SO_2 from reaching the sorbent pores and reacting. With injection through tertiary or overfire air ports, the limestone particles are allowed to cross the flame without crossing the highest temperature zone.[9] This aids in producing inert calcium compounds which can be removed in a particulate collection device and disposed of in an environmentally acceptable manner. These calcium compounds are formed in proportion to both sulfur content in the fuel and calcium-to-sulfur molar ratios for the sorbent injection process.

Figure 11 shows a conceptual view of the LIMB process. The limestone is calcined rapidly to lime which then combines with SO_2 to form calcium sulfate. The chemical reactions are shown in the following equations:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1}$$

$$CaO + SO_2 + \tfrac{1}{2} O_2 \rightarrow CaSO_4 \tag{2}$$

The sorbent should be in the gas temperature regions above approximately 2200°F for a very short period of time to prevent deactivation or deadburning. Conversely, the limestone will only minimally calcine below approximately 1400°F. The optimum then is to produce sufficient residence times in the 2200°F to 1400°F temperature zone within the boiler.[10] This temperature zone usually occurs between the entrance to the radiant superheaters to a point approximately half way through the convection passes of the boiler, as noted in Figure 12. Typical residence times in these areas are from 1 to 2 seconds, depending on the unit design, the slagging and fouling characteristics of the fuel being burned, the erosion and corrosion tendencies, and fan capabilities. Some units, especially in the mid to late 1960s, were being designed in a very competitive market, and fewer leeways were incorporated in an attempt to keep costs down.

New unit designs are more conservative with larger furnaces and lower heat release rates to accommodate low-NO_x burner requirements. Also, the use of Western subbituminous fuels with their inherently high ash content has necessitated wider tube spacings and lower velocities through the tube bundles. New unit designs lend themselves well to the sorbent injection technology.

The calcination reaction is endothermic, which means that the process will absorb heat during the reaction. The heat required for calcination of pure limestone is approximately 2,000 Btu/lb. The sulfation process is exothermic and releases approximately 4,000 Btu/lb of lime (CaO). However, only about ½ lb of CaO is produced for every 1 lb of limestone, and only 25 percent of this is sulfated. This can result in a small energy penalty and reduce overall flue gas temperatures slightly.

Based on a 10^6 lb/hr steam boiler with turbine conditions of 1000/1000°F and 2400 psi throttle pressure, approximately 25,800 lb/hr of limestone is required, based on a high (3.4 percent) sulfur Midwestern bituminous coal, to produce a Ca/S molar ratio of 2. The basic quantities for these conditions are tabulated below. It is readily apparent that the ash quantities passing through the unit under these conditions are more than doubled.

Basic Quantities

Main steam flow	1,000,000 lb/hr
Reheat steam flow	853,900 lb/hr
SH/RH outlet steam temperature	1005°F
Turbine throttle pressure	2400 psig
Fuel flow	128,000 lb/hr
Fuel ash flow	10,750 lb/hr
Sorbent flow	25,800 lb/hr

Note: Coal fuel—10,650 Btu/lb HHV
3.4% S
8.4% Ash

This high ash quantity can affect heat transfer within the boiler in different ways. High ash loadings can affect flue gas emissivities as well as physically blocking radiation which might normally go to the waterwalls. In addition, the added particulate loading may increase slagging tendencies within the furnace. This slag layer can reduce the heat absorption in the waterwalls, preventing absorption in the generation side of the steam process. Field tests performed approximately 15 years ago did not reveal any significant problems due to slagging because of the addition of sorbent injection. However, there is only a limited amount of data, and some questions have been raised as to whether or not the units were on line long enough to produce slagging problems. More information is needed to be able to predict the slagging tendencies of various coals with sorbent injection with any degree of certainty.

The increased flyash quantities produced by sorbent injection can also affect fouling tendencies of the fuels. Again, the results of the field tests some 15 years ago are inconclusive, showing influences of limestone injection on fouling from slight to severe. Some of the deposits were hard and difficult to remove while on other units there were more deposits but they were softer in nature and easily removed. In general, however, fouling deposits are increased because of the increase in particulate flowing over the convection surface. For existing units, increased numbers of soot blowers, increased blowing pressures, or increased blowing frequency may be needed to handle increased ash flows. For new units, the tube spacing in a transverse direction from side to side can be increased, preventing the fouling buildups from plugging the convection passes by bridging over between the various assemblies of tubes. While increased tube spacing will not prevent fouling, it does allow more time between soot blowing cycles so that the gas flow lanes can be kept open (see Figure 13).

Erosion tendencies are increased with the higher loading of particulate in the flue gases. For existing units, this can be troublesome because of the difficulty in altering heat recovery surface spacing and configuration while still maintaining adequate heat transfer surface to perform the required duty. Shields can be installed on tubes but these are only a temporary stopgap and the erosion will continue, making the shields a maintenance item. For new units, the designs can incorporate wider tube spacings or increased depth of the gas passages to bring flue gas velocities down to a safe level. Below 3600 ft/min, erosion tendencies are generally negligible based on the design of the unit and the turns which the flue gases must make before entering a bank of superheater, reheater, economizer, or other heat recovery tubes.

The increased particulate loading also has an adverse effect on air preheaters. The tight spacing of preheater baskets can lead to pluggage because of the increased dust loadings. More material is deposited on the plates, and bridging between the heat transfer elements is increased. As with the convection passes, part of this pluggage can be attributed to a lowering of the ash sintering temperature by the sorbent ash particles.

Bottom ash quantities and bottom ash removal may not be adversely affected by sorbent injection. In general, the limestone will be injected around or above the burners and conceivably in a much finer size than pulverized coal. It is expected that this small, lighter material will be swept upward with the flue gases, especially if injected above the burners through overfire air ports, and not increase the amount of ash in the bottom of the furnace hopper.

A complementary technology that may substantially decrease the concerns about particulate flows from the LIMB process is coal cleaning. This process, one study of which is now underway at EPRI's Waltz Mill facility, can substantially reduce the ash and sulfur content of the coal fuel. Ash and sulfur removals of 70 and 30 percent, respectively, have been reported. These reductions tend to cancel out the additions to solid waste flows associated with sorbent injection.[11]

EFFECT ON BALANCE OF PLANT

Sorbent Handling

One of the major impacts of retrofitting LIMB to an existing plant is the need for a sorbent handling system. Based on the 10^6 lb/hr boiler discussed earlier, which burned 3.4 percent sulfur coal with a Ca/S molar ratio of 2, approximately 25,800 lb/hr (as limestone) is required at the boiler. Although optimum sorbent selection criteria, including grind size, are the subject of continuing research, it is expected that a high surface area (i.e., high reactivity) stone will be required, finely ground to approximately 90 percent passing through a 325 mesh screen.

It is expected that most retrofit plants would receive the sorbent by truck. It would be stored in a pile with a roof over it to prevent unnecessary moisture contamination. Depending on the as-delivered size and moisture content of the stone, it may then require crushing to an intermediate size (3/8 to 3/4 x 0 in.) and drying prior to final fine grinding. Candidate mills for pulverization include ball, roller, high speed hammer, attrition, and pin mills. Grinding power to produce a finely ground product such as 20 μm mean size will be high. Agglomeration of finely ground sorbent accompanied by its adherence to inner mill surfaces and consequent reduced mill efficiency, is a known problem. If an extremely fine sorbent is necessary, it may become appropriate to consider other grinding techniques.

Following final milling, the sorbent would be stored in one or more outside day silos and would be pneumatically injected into the furnace. The pneumatic system is expected to be dilute phase with fairly high injection velocities to promote adequate penetration and dispersion within the furnace.

Special care would have to be taken with the design of equipment handling the finely ground product because of its agglomeration tendencies. Silos, for example, would be mass flow design with slot bottoms to prevent bridging. Heating would be provided where necessary to prevent condensation. For extremely fine sorbent, it may be better to directly inject the product as it leaves the mills to avoid silo storage.

It is expected that new units would have similar sorbent systems. Some units would have provisions for rail or barge delivery of sorbent, and portions of the receiving facility might be used in common with the coal handling system.

Particulate Removal

A second major impact of retrofitting LIMB to an existing plant is a markedly increased flue gas particulate loading. For the 10^6 lb/hr steam boiler discussed earlier, the flyash load increased by a factor of 2.4. This assumes a finely ground sorbent, essentially all of which is entrained in the flue gas. Although flyash particle size distribution is expected to change very little, earlier tests[1] have indicated increases in resistivity by about two orders of magnitude. These factors present problems for older installed precipitators, most of which have specific collecting areas (SCAs) well below 400 ft^2/1000 acfm. Many of these units would require renovation, expansion, and/or flue gas conditioning to maintain effective particulate removal.

It is believed that SO_3 injection can effectively reduce resistivity to manageable levels on retrofits. There are also several older plants that have recently been retrofitted with larger precipitators. These units may be able to handle increased LIMB ash loading without conditioning and without major modification. The use of cleaned coal together with LIMB could prove to be an economical retrofit solution in precipitator-limited cases.

New unit applications are expected to favor the use of fabric filters which would be insensitive to the increased resistivity. Fabric filters could also see application on some retrofits in combination with an existing precipitator, should this approach prove economically attractive.

Ash Handling and Removal

The increased fly ash loading affects the ash handling equipment of the particulate removal device as well. Necessary modifications to this system on a retrofit may include larger size and/or increased number of precipitator hopper ash removal lines and increased capacity pressure or vacuum producing equipment, including any added support facilities/systems required. Larger or added ash silos would be required, as well as provision for dry handling of the alkaline ash because of its cementitious properties.

Since essentially all sorbent injected into the furnace is expected to be entrained in the flue gas, the bottom ash system should see minimal impact. Any sorbent in the bottom ash is expected to be sintered and relatively unreactive; however, bottom ash sluice/pond water pH would require scrutiny, and suitable pH controls should be installed, if necessary.

The ash disposal site envisioned would consist of a properly designed landfill, although possibilities for commercial use of the product (e.g., as an aggregate fill) exist as well. Although there is little data on hazards associated with LIMB ash disposal, it has been found that ash in alkaline matrices, including fluidized bed combustion ash and dry scrubber ash has, in general, not presented hazardous leachate problems. More research may be necessary to resolve this issue for LIMB.

As in the case of the particulate removal equipment, the use of lower ash content or cleaned coal would help reduce the impact of LIMB on the ash handling system by reducing overall ash quantity.

Sorbent Postcombustion Treatment

In order to achieve 70 to 90 percent SO_2 reduction, as required by NSPS on new units, LIMB (in combination with additional sorbent post combustion treatment devices) may be necessary. With this configuration, LIMB would capture the majority of the SO_2 in the furnace and provide a highly reactive calcined sorbent product in the flyash that could be effectively used by a downstream device such as a spray dryer. It is anticipated that the flyash would be caught in a mechanical collector, slurried, and sprayed into the absorption chamber of the spray dryer where about 80 percent or more capture of the inlet SO_2 is possible.[12] A fabric filter would be used for final particulate removal, and this could contribute to another 5 to 20 percent inlet SO_2 capture.

The combination of these SO_2 capture techniques would result in the NSPS-required 70 to 90 percent SO_2 reduction in what is expected to be a cost-effective manner. The system could be optimized by bypassing a portion of the flue gas stream around the spray dryer to the extent that the required SO_2 capture is achieved. This would reduce spray dryer costs and avoid the need for flue gas reheating. Operating costs are expected to be comparatively low because the equipment is relatively uncomplicated and the sorbent (assuming limestone) cost is low.

Soot Blowing

As discussed earlier, LIMB retrofits are expected to require additional soot blowers to control fouling. Also, the required blowing pressures and blowing frequencies may have to be increased. Either air or steam soot blowers may be used. If air is the selected medium, new soot blowing air compressors and distribution systems would be required at many installations. Steam soot blowing may prove to be a more economical solution in many cases.

COST

EPRI has estimated the incremental cost of LIMB on new units equipped with fabric filters to range from $15 to $30/kW, depending on coal sulfur content and Ca/S molar ratio.[4] Retrofits could cost two to three times as much to account for upgrading of soot blowing, precipitators, and ash handling and disposal systems. EPRI estimates 30-year, levelized operating costs of 3 to 12 mills/kWh, depending on coal sulfur content and required Ca/S molar ratio.

More detailed cost estimates are currently being prepared by the authors of this paper and others on behalf of the EPA. These estimates will address a wide range of utility plant sizes, both new and retrofit, with high and low sulfur coals. It is expected that these estimates will confirm that the cost of LIMB will be at least $100/kW less than that for scrubbers.

CONCLUSIONS

Sufficient field information is not available on sorbent injection to determine its effectiveness as a viable means of reducing air pollutants. Full-scale demonstrations of the sorbent injection process using various coals, sorbents, and boiler designs, could provide this information.

An area of concern is not whether sorbent injection can remove SO_2 before the flue gases discharge into the atmosphere from the stack, but rather how much of the SO_2 can be removed. This paper has noted various areas which must be considered in any sorbent injection installation. These include sorbent handling and injection, fouling in the convective passes and air preheaters, particulate removal in electrostatic precipitators or fabric filters, and disposal of the products of combustion and sorbent injection. Although these concerns are significant, the alternatives to sorbent injection for SO_2 removal may be more costly and present more problems. LIMB technology offers the potential for low cost reductions in NO_x and SO_2 in response to acid rain concerns, and this should be evaluated carefully for both retrofit and new units.

AKNOWLEDGEMENT

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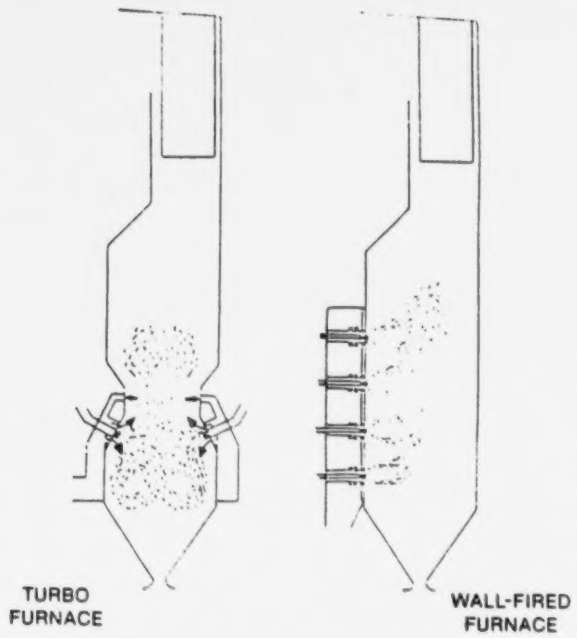

TURBO FURNACE
WALL-FIRED FURNACE

Figure 1. Riley Coal-fired Boiler Designs

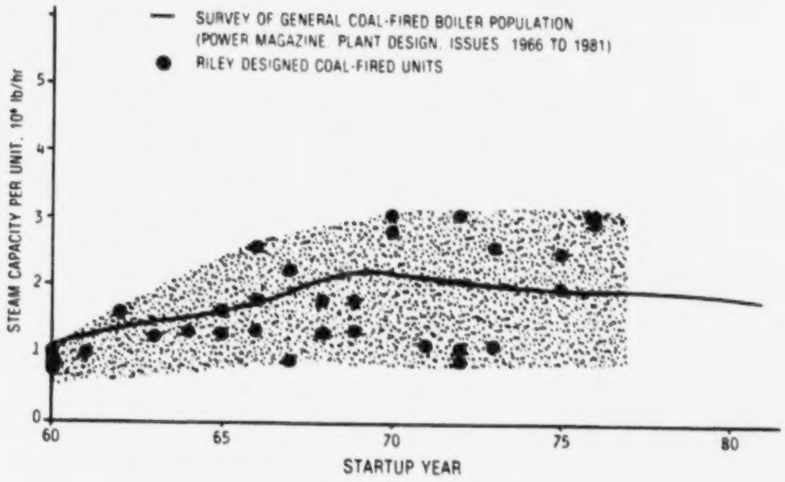


Figure 2. Steam Capacity vs. Startup for Riley Wall-fired Units

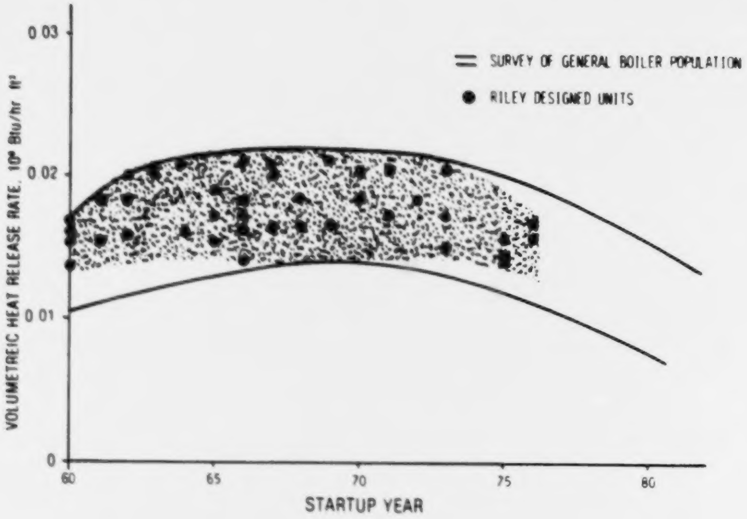
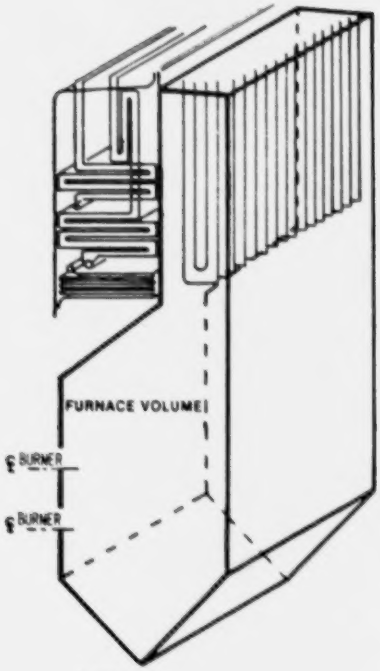


Figure 3. Volumetric Heat Release vs Startup Year for Riley Wall-fired Units


FURNACE VOLUME
℄ BURNER
℄ BURNER

NOTE
FURNACE VOLUME IS FIGURED TO
THE FURNACE EXIT PLANE MINUS
THE VOLUME OF THE RADIANT
SUPERHEATER TUBES

Figure 4. Illustration of Furnace Volume for Heat Release Calculations

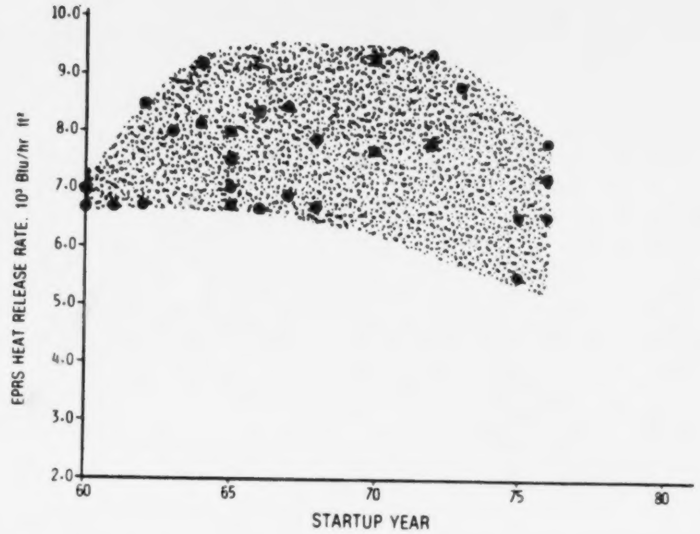


Figure 5. EPRS Heat Release Rate vs. Startup Years for Riley Wall-fired Units

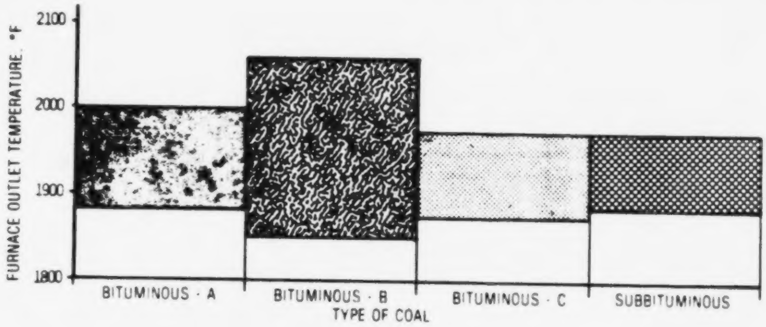


Figure 6. Furnace Outlet Temperature vs. Type of Coal for Riley Designed Units

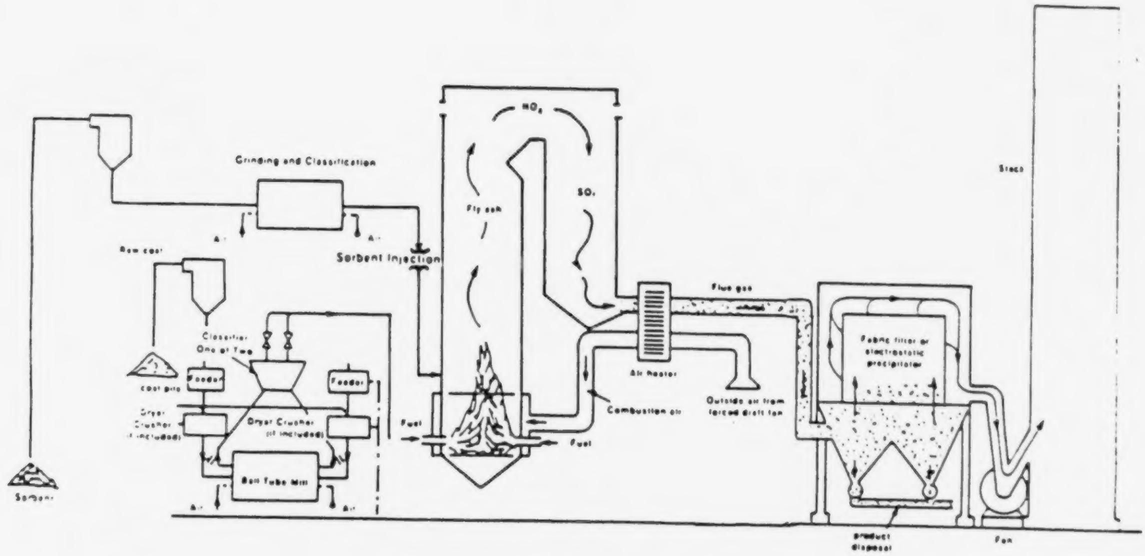

NO$_x$
SO$_x$
Fly ash
Grinding and Classification
Air
Air
Raw coal
Sorbent Injection
Classifier One of Two
Coal pile
Feeder
Feeder
Dryer Crusher (if included)
Dryer Crusher (if included)
Ball Tube Mill
Air
Air
Sorbent
Fuel
Fuel
Combustion air
Air heater
Outside air from forced draft fan
Flue gas
Fabric filter or electrostatic precipitator
Stack
product disposal
Fan

Figure 7. LIMB System Schematic

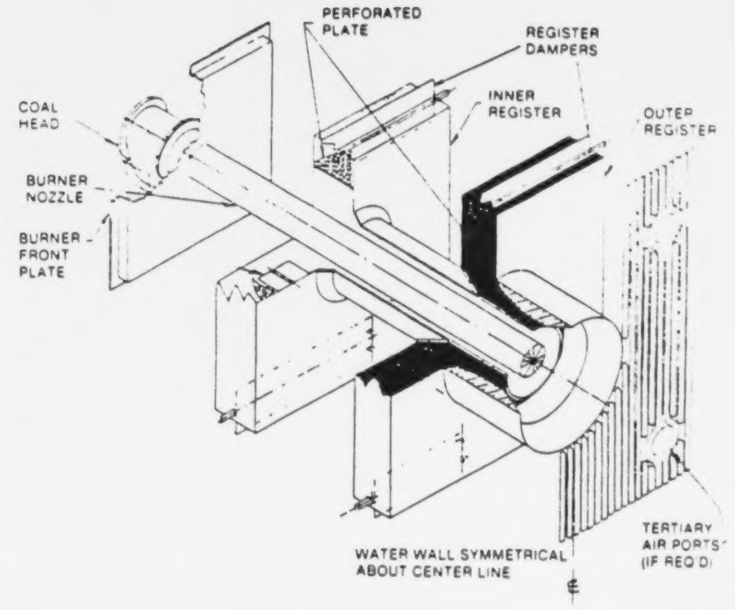

PERFORATED PLATE
REGISTER DAMPERS
INNER REGISTER
OUTER REGISTER
COAL HEAD
BURNER NOZZLE
BURNER FRONT PLATE
TERTIARY AIR PORTS (IF REQ'D)
WATER WALL SYMMETRICAL ABOUT CENTER LINE
℄

Figure 8. Riley Stoker Distributed Mixing Burner

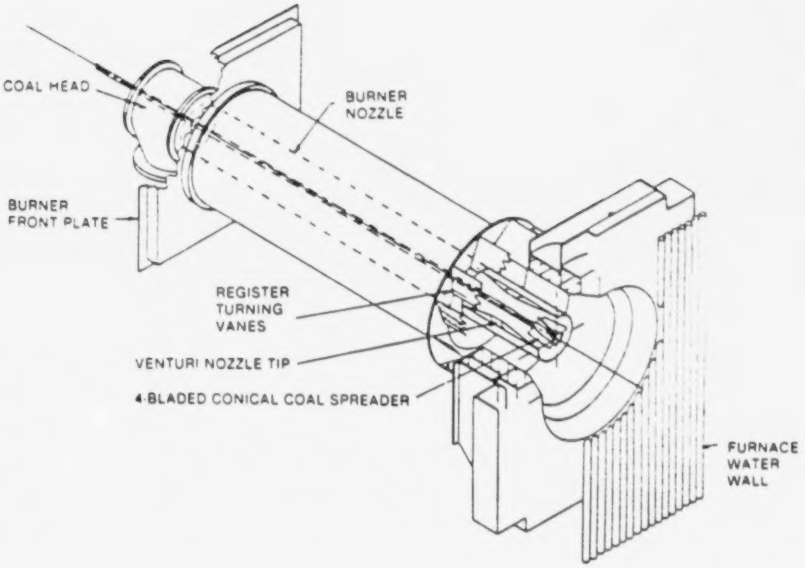
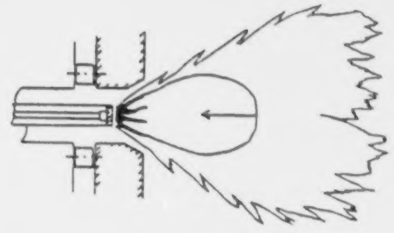
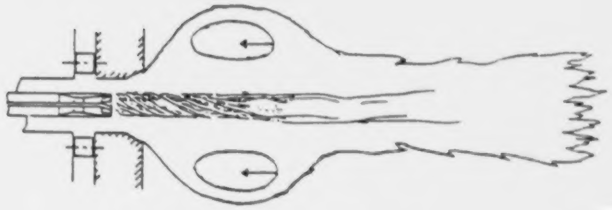

COAL HEAD
BURNER NOZZLE
BURNER FRONT PLATE
REGISTER TURNING VANES
VENTURI NOZZLE TIP
4-BLADED CONICAL COAL SPREADER
FURNACE WATER WALL

Figure 9. Riley Stoker Controlled Combustion Venturi (CCV) Burner



FLARE-TYPE BURNER



CONTROLLED COMBUSTION VENTURI BURNER

Figure 10. Typical Flame Shapes

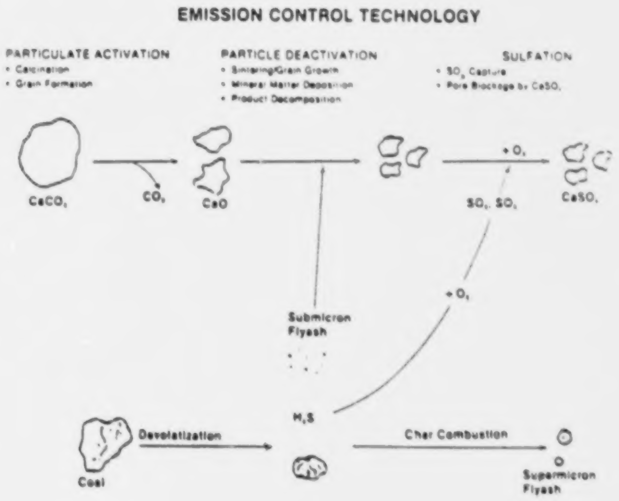

EMISSION CONTROL TECHNOLOGY
PARTICULATE ACTIVATION
• Calcination
• Grain Formation
PARTICLE DEACTIVATION
• Sintering/Grain Growth
• Mineral Matter Deposition
• Product Decomposition
SULFATION
• SO_x Capture
• Pore Blockage by $CaSO_4$
$CaCO_3$
CO_2
CaO
$+O_2$
SO_2, SO_3
$CaSO_4$
$+O_2$
Submicron Flyash
H_2S
Coal
Devolatization
Char Combustion
Supermicron Flyash

Figure 11. Limestone Transformations in a Pulverized-Coal Flame

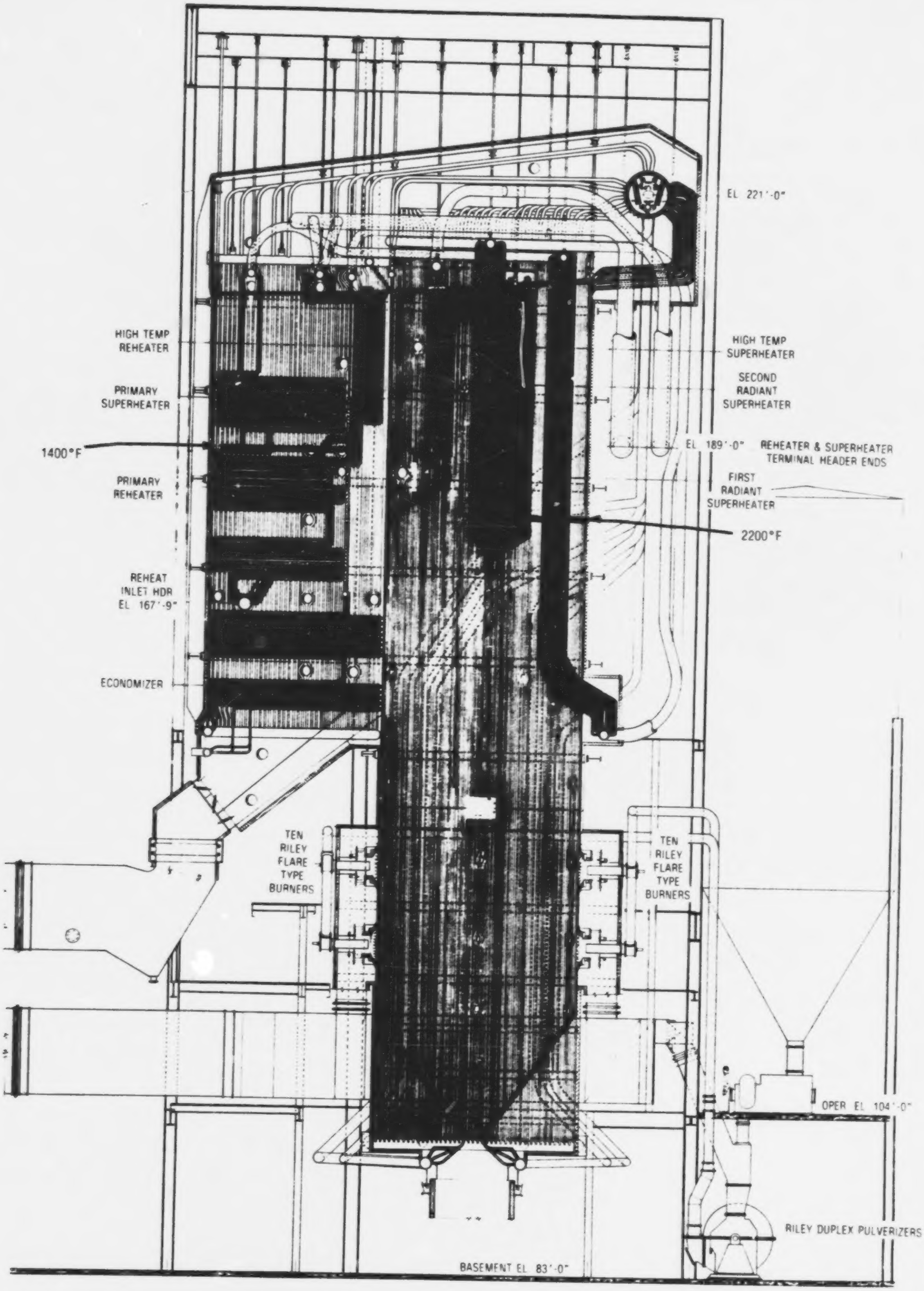

HIGH TEMP REHEATER
PRIMARY SUPERHEATER
1400°F
PRIMARY REHEATER
REHEAT INLET HDR EL 167'-9"
ECONOMIZER
EL 221'-0"
HIGH TEMP SUPERHEATER
SECOND RADIANT SUPERHEATER
EL 189'-0"
REHEATER & SUPERHEATER TERMINAL HEADER ENDS
FIRST RADIANT SUPERHEATER
2200°F
TEN RILEY FLARE TYPE BURNERS
TEN RILEY FLARE TYPE BURNERS
OPER EL 104'-0"
RILEY DUPLEX PULVERIZERS
BASEMENT EL 83'-0"

Figure 12. Approximate Temperature Zone for Optimum Sorbent Reaction

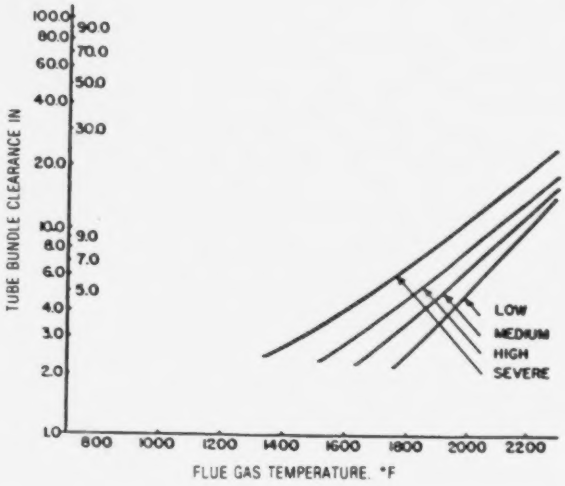


Figure 13. Tube Bundle Clearance vs. Flue Gas Temperature for Different Fouling Potential Coals

DRY SORBENT EMISSION CONTROL PROTOTYPE CONCEPTUAL DESIGN AND COST STUDY

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ABSTRACT

The Dry Sorbent Emission Control (DSEC) program conducted by the Electric Power Research Institute (EPRI) is aimed at developing the DSEC technology in three successive steps: a fundamental pilot- and bench-scale test program, a prototype or intermediate-scale test program at a small production boiler, and a full-scale demonstration at a 400-MW or larger utility boiler. The first step of this process has been in progress since mid-1983 under the joint sponsorship of EPRI and Southern Company Services (SCS), Inc. One product of the current program is a conceptual design and cost study for a one- to two-year prototype evaluation of DSEC technology at a 40-MW utility boiler. This paper reports the results of the prototype study, which is based on Gulf Power Company's Plant Scholz Unit 2. A prototype design based on an evaluation of major process performance and engineering issues is described. Estimated capital and O&M costs for the prototype are presented. A feature of the study is its organization by process subsystems, which allows a variety of test scenarios to be constructed. The projected capital cost of an alternate test scenario is reported.

INTRODUCTION AND BACKGROUND

Outline of the DSEC Process

The potential effects of "acid rain" legislation on the electric utility industry have spurred the investigation of a range of technologies for retrofit SO_2 control, including alternatives to flue gas desulfurization by means of wet scrubbers. As part of this investigation, Southern Company Services (SCS), Inc., on behalf of the operating companies of the Southern electric system, has teamed with the Electric Power Research Institute (EPRI) to examine a process that has been named Dry Sorbent Emission Control (DSEC). DSEC in its fullest form is an integrated process for the control of SO_x, NO_x, and particulate emissions. As such, it consists of the following steps:

- Boiler limestone (or lime) injection for SO_2 control.
- Low-turbulence burners for NO_x control.
- Sodium addition between the air preheater and baghouse for supplemental SO_2 control.
- A baghouse for particulate and final SO_2 control.

As a practical matter, some of these steps may be omitted in specific retrofit applications because of technical, economic, or compliance considerations. Based on development work by EPRI and SCS, low-NO_x burners are not considered necessary for in-furnace SO_2 control. The implementation of post-furnace sodium injection requires that a baghouse be included to achieve acceptable utilization of the sodium-based sorbent.

The DSEC development program is aimed primarily at the investigation of in-furnace sorbent injection as the major SO_2-control step in the process. This emphasis is reflected in the present paper. Tests of the sodium injection step conducted by EPRI at Public Service Company of Colorado's Cameo Station achieved SO_2 removals from 40 to 60 percent with trona at a Normalized Stoichiometric Ratio (Na_2:S) of 1 to 1.1. However, the use of sodium compounds is assumed to be constrained in an Eastern application of DSEC because of waste disposal considerations.

DSEC Program Description and Status

In April, 1983, SCS submitted a proposal to EPRI for the joint development of the DSEC process. This proposal was accepted by EPRI in late 1983. While the SCS proposal focused primarily on a pilot-scale development effort, it also outlined a long-range program for development of the process to commercialization in a timely manner. The proposed development program consists of two steps beyond the pilot scale: a prototype evaluation at a small production boiler (20-80 MW), and a full-scale demonstration program at a large (400+ MW) utility boiler. The prototype is considered a necessary intermediate step to effect a reasonable scale-up of the technology before placing a large utility boiler at risk.

At the time of presentation of this paper, the joint EPRI/SCS DSEC pilot program has been in progress for over a year. Extensive furnace sorbent injection tests have been conducted in Southern Research Institute's (SRI) 10^6-Btu/hr research combustor in Birmingham, Alabama, and supporting bench-scale tests have been carried out by KVB, Inc., of Irvine, California. In parallel with the experimental work at SRI and KVB, SCS has initiated planning for a 40-MW prototype evaluation of DSEC at Gulf Power Company's Plant Scholz located near Sneads, Florida. The present paper summarizes the results of SCS's conceptual design and cost study for the Plant Scholz prototype. It must be emphasized that the prototype conceptual study was conducted as a planning tool for the primary benefit of SCS and EPRI and is strictly applicable only to a prototype program at Plant Scholz. Other utilities should approach the design of a dry sorbent injection prototype facility differently based on their own requirements.

PROTOTYPE DESIGN APPROACH

The prototype research facility design presented in this paper reflects a number of both technical and "philosophical" considerations. A discussion of these considerations will be helpful in evaluating the process design presented subsequently. The major factors that have shaped the prototype design are: (1) the implications of the EPRI/SCS pilot program results, (2) an assessment of major engineering and operational issues important for process commercialization, (3) a consideration of DSEC solid waste disposal issues, and (4) past SCS prototype test experience.

Implications of the Pilot Work

The EPRI/SCS pilot tests conducted at SRI's Coal Combustion Research Facility are aimed at quantifying the effects of a number of process parameters on in-furnace sulfur removal. Parameters investigated to date have included sorbent type, calcium/sulfur ratio, limestone particle size, fuel type, time/temperature history (through load and injection location), jet mixing, and combustion zone stoichiometry (staged combustion). The most important conclusions from the standpoint of the prototype design can be summarized under three headings: SO_2 removal efficiencies, time/temperature effects on calcination and sulfation, and the influence of sorbent characteristics.

SO_2 Removal Efficiencies. The EPRI/SCS pilot work to date has indicated that a calcium-to-sulfur ratio of 2.5 to 3 may be necessary to achieve 50-percent SO_2 removal with limestone. For hydrated lime, removals of 50 to 60 percent are possible at a Ca/S ratio of 2. Dolomite and dolomitic hydrated lime have demonstrated higher calcium utilizations in the pilot tests, but these sorbents offer no advantage over limestone and hydrated lime on a mass or sorbent cost basis.

In order to meet a 50-percent reduction target, the Plant Scholz prototype design is based on a maximum calcium-to-sulfur ratio of 3 with limestone for a coal containing 3.5 percent sulfur. The system designed on this basis is readily adaptable to the handling of hydrated lime and prepulverized limestone. The effects of high sorbent loadings on the boiler and its auxiliaries, and increased capital and operating costs argue against designing the prototype system for feed rates greater than Ca/S=3.

Time/Temperature Effects. The fundamental mechanisms which govern the capture of sulfur dioxide by calcium in the furnace are still under investigation in the EPRI/SCS pilot program. However, it appears from work to date that there is an injection region in the furnace which maximizes the sulfur capture efficiency of a given sorbent. For both limestones and hydrated limes, this maximum generally occurs at injection locations downstream of the flame zone corresponding to peak injection temperatures between 1800°F and 2300°F. This effect is illustrated for two limestones and one hydrated lime in Figure 1.

While a full discussion of the phenomenon shown in the figure is beyond the scope of this paper, the following conclusions have a direct effect on the prototype design:

- The primary mechanism of sulfur capture is through the reaction of calcium oxide and sulfur dioxide in the presence of oxygen rather than through a reducing zone mechanism in the flame zone.
- For injection at temperatures above 2300°F, loss of sorbent reactivity (as measured by BET surface area) is very rapid due to an increase in the rate of sintering (merging of calcium oxide crystals) as temperature increases.
- The sulfation reaction is thermodynamically unfavorable above approximately 2400°F; therefore, residence time above this temperature does not contribute significantly to sulfation.
- At temperatures below approximately 1800°F, both calcination and sulfation rates slow markedly. This is compounded by the fact that useful residence time becomes very limited when sorbent is injected below 1800°F (e.g., less than 1 second in the SRI combustor).

- Between approximately 1800°F and 2300°F, tradeoffs among calcination rate, development of sorbent reactivity, sulfation kinetics, and useful residence time for sulfation determine an optimum calcine utilization. The precise optimization point varies with sorbent type and sorbent properties.

Based on these conclusions, the following design decisions were made for the Plant Scholz prototype: (1) Sorbent will be injected in the upper furnace (below 2300-2400°F) for maximum SO_2 control. (2) Several injection levels between approximately 2400°F and 2000°F will be included to allow for optimization of sorbent utilization over a range of boiler loads. (3) Lower-furnace injection (including injection through the burners) will be excluded. (4) Low-NO_x burners do not appear to be necessary for optimization of sulfur capture and will not be installed.

Sorbent Type and Properties. A range of sorbent-related parameters has been investigated in the EPRI/SCS pilot program. The most important parameters to date have been sorbent type (e.g., limestone, hydrated lime), chemical and morphological properties, and particle size (particularly for limestones). With regard to sorbent type, the ranking of various sorbents from higher to lower average calcium utilization under similar conditions is as follows: hydrated dolomitic lime, hydrated lime ($Ca(OH)_2$), dolomite, and limestone. (However, note that this is also the ranking of the sorbents from higher to lower cost per mole of calcium).

Differences in performance due to chemical and morphological properties were found primarily among limestones. For example, the two limestones shown in Figure 1 differ significantly in percent insolubles, grain size, degree of crystallinity, and initial surface area. Some of the evident differences in performance are apparently attributable to these factors.

Limestone particle size exhibits a strong effect on sulfur capture efficiency, particularly as mass mean diameter (MMD) falls below approximately 10 microns. In a recent series of experiments, utilizations ranged from approximately 20 percent to nearly 40 percent as the limestone particle mass mean diameter dropped from 15 microns to under 0.1 microns. From a practical standpoint, the cost of fine grinding limestone undoubtedly becomes prohibitive at some mean particle size. However, the ultimate tradeoff between grinding costs and process efficiency cannot be fully evaluated without testing in the field.

In sum, sorbent-related parameters have implications for the design of a prototype test facility. Ideally, such a facility should be designed for flexibility with respect to sorbent type and properties. This includes the ability to receive and test a variety of hydrated limes and limestones which vary in cost, geographical location, and commercial availability. Because relatively few limestones are available in prepulverized form, on-site pulverization equipment may be required to test those limestones of most interest to utilities. On-site pulverization also allows the tradeoffs between particle size effects and grinding costs to be evaluated at an appropriate scale.

Engineering and Operational Issues

The true commercial potential of a process such as DSEC depends not only on the process science but also on the engineering embodiment of the technology and the effects of the process on power plant performance. The prototype facility described in this paper is designed to allow the evaluation of the most important engineering and operational issues from the processing and storage of sorbents to the disposal of the process waste product. These issues include the following:

- Reliability and operation of materials handling systems and the integration of these systems with boiler operation over a range of boiler loads.

- Feasibility, cost, and reliability of limestone pulverization.

- Long-term effects of furnace sorbent injection on the boiler and its auxiliaries, particularly in the areas of slagging, fouling, plugging, corrosion, and boiler efficiency.

- Effects of sorbent injection on precipitator performance, and means of compensating for the expected decrease in precipitator efficiency.

- Effects of sorbent injection on baghouse performance, particularly in the areas of baghouse pressure drop, filter cake characteristics, cleaning cycles, and bag life.

- Characteristics of the DSEC waste product and evaluation of waste disposal options with respect to feasibility and cost.

The decision to design the Plant Scholz facility to examine issues such as these has several implications. First, there is the obvious effect on the scope and type of equipment specified in the design. For example, the evaluation of on-site limestone pulverization adds significantly to the prototype equipment list and cost. Second, most of the issues mentioned above require an extended test period for thorough evaluation. This in turn calls for the specification of process equipment that will perform satisfactorily over the duration of the test period, as well as adding to total project O&M costs.

DSEC Waste Disposal

Another important factor addressed in the Plant Scholz prototype design is disposal of the waste solids produced by the DSEC process. The waste resulting from dry sorbent injection has several characteristics that make it fundamentally different from typical Eastern bituminous coal ash. These include:

- High levels of alkaline compounds, including large amounts of free lime (CaO).
- Cementitious behavior in contact with moisture.
- Relatively high water solubility of certain constituents.

The chemical and physical properties of the DSEC waste will vary depending on a number of factors. Generally, the chemical properties are expected to be similar to those of the waste from a high-sulfur spray dryer application. The physical properties are expected to be similar to those of high alkalinity lignitic coal ash. As an example, the pH of the DSEC waste is expected to be above 10 and as high as 13 depending on the level of available alkalinity. The mobility of metal ions from the waste when placed in a disposal site will be a complex function of a number of factors including pH, coal composition, and free lime content, among others. Post-furnace sodium injection further complicates waste disposal due to the high solubility of sodium compounds. Because of these characteristics of the DSEC waste and the increasing emphasis on waste disposal regulations and groundwater protection measures at the federal and state levels, landfill disposal has been specified in the Plant Scholz prototype design. The disposal area design provides for isolation of the sodium-containing waste, a runoff ditch system and holding pond, and a series of monitoring wells to facilitate evaluation of the landfill disposal method.

SCS Prototype Test Experience

Finally, the prototype conceptual design reflects a test philosophy developed by SCS through experience with several prototype test programs. One such program was the evaluation of three FGD prototypes conducted at Plant Scholz during the 1970's. Two major conclusions concerning test approach have emerged from these programs. First, SCS's experience has demonstrated the advantages of specifying test equipment whose performance and operation will readily scale to the next level of development. The added investment in capital cost can yield valuable process information that will reduce costs and development time in future process scale-ups and provide meaningful data for the refinement of process economics. Second, SCS experience points to the importance of designing a test system for test continuity and flexibility. Design short-cuts on the front-end of a test program may result in poor equipment reliability, poor data quality, or the inability to change test procedures as the test program evolves.

Summary of the Plant Scholz Design Approach

The previous paragraphs have provided some background on the design decisions made for the Scholz prototype. The preliminary conclusions drawn from the DSEC pilot work call for upper-furnace injection of sorbent at multiple boiler levels and rule out the necessity of low-NO_x burners for SO_2 removal. The effects of sorbent differences on SO_2 removal efficiency call for flexibility in receiving and processing sorbent materials, including on-site pulverization of limestone. The importance of engineering and operational issues for the success of the DSEC process broadens the scope of the research program and dictates a process design similar to that which might eventually be applied in a commercial facility. A landfill waste disposal system is included in the conceptual design based on a consideration of the nature of the DSEC waste product. Finally, SCS's experience in designing and conducting prototype test programs places emphasis on design flexibility and the specification of utility-grade equipment to assure test continuity and quality data.

DETAILS OF THE PROTOTYPE CONCEPTUAL DESIGN

Design Basis and Criteria

The design approach described above was applied to a conceptual design for a prototype DSEC test facility at Gulf Power Company's Plant Scholz. This plant consists of two identical Babcock & Wilcox boilers with nameplate ratings of 40 MW. The boilers, which began commercial operation in 1953, were designed for steam throttle conditions of 900°F and 850 psig with a boiler rated capacity of 425,000 pounds of steam per hour. Unit 2 was chosen for the design study because it is the host unit for the EPRI/SCS high-sulfur-coal pilot baghouse, which provides an ideal opportunity to test the integrated DSEC concept. Features of Plant Scholz include a wide load range (20 to 48 MW), good control of steam temperature by flue gas recirculation and superheater bypass, and a large cold-side electrostatic precipitator (544 ft^2/kcfm), as well as a long history of involvement in research programs.

Table 1 lists the major design criteria used to size the equipment for the conceptual design. The coal specified for the study is a hypothetical 3.5-percent-sulfur bituminous coal such as might be found in the Illinois Basin. Sorbents used in the study include limestone and hydrated lime for furnace injection, and trona, a naturally occurring sodium-based compound originating in the Western United States, for injection ahead of the slipstream baghouse. Table 1 also lists the design reactant/sulfur molar ratios and SO_2 removal efficiencies. The stoichiometries specified are the peak stoichiometries to be tested under the design conditions (40 MW, 3.5-percent-sulfur coal) and are not necessarily representative of economically or technically acceptable performance for the commercial technology.

Table 2 summarizes the operating basis and storage capacities for process equipment and areas. Raw limestone handling and waste disposal are assumed to operate with one shift per day to reduce manpower requirements and avoid nighttime operation of mobile equipment. The limestone receiving hopper and solid waste storage silo are given sufficient storage capacity to allow for continuous testing throughout the unmanned shifts. The pulverized limestone/lime silo is sized to accommodate the receiving and storage of preprocessed sorbents such as prepulverized limestone or hydrated lime. Waste landfill areas are sized for a combined total of two years of waste production at 60 percent of the process design point. This provides for an extension of the test program beyond one year without new construction.

Process Design

The general design criteria were used to define the conceptual process design for the prototype facility. The process flow diagram (PFD) in Figure 2 shows the major equipment and process flows. Equipment items are identified more specifically in Table 3, and continuous process flow streams are quantified in the material balance given in Table 4. Five process subsystems are identified in the PFD. Three additional subsystems not identified in the PFD provide general support for the process. Following is a brief description of each of the subsystems. Equipment numbers mentioned in the text refer to designations in the PFD and Table 3.

Limestone Handling and Pulverization. The purposes of this subsystem are to receive, store, dry, and pulverize crushed limestone and deliver the pulverized product to storage. The crushed limestone (nominally 3/4" x 0") is stored in two 15-day piles, one of which is covered to provide sufficient residence time for partial drying. The crushed limestone is transferred by a front-end loader from the covered pile to a bucket elevator (E-101), which fills the 150-ton hopper (H-101). The 150-ton hopper provides some 20 hours of limestone feed to the pulverizer at the process design flow of 6.7 tons of dry limestone per hour. The pulverizer is a roller-and-race type vertical-spindle mill with internal classifier sized to produce 10 tons per hour of limestone at finenesses up to 90 percent passing a 325-mesh screen. The grinding process used here is a closed-circuit grinding approach in which the pulverized limestone is recycled until the desired fineness is achieved. The pulverized product is separated from the mill air by a primary cyclone and bag filter and emptied into a small feed hoper (H-102) which supplies a gravimetric feeder. From this hopper, the limestone may be loaded pneumatically into a storage silo or conveyed to the boiler for direct injection.

Pulverized Sorbent Storage and Conveying. The purpose of this subsystem is evident from the title. The heart of the system is a 500-ton storage silo (S-102) supplied from pulverizer P-101 and a 2000-scfm sorbent conveying and injection blower (B-102) which pneumatically transports the pulverized sorbent to the boiler injection system. Also included in this system is a weigh-belt feeder which is the primary metering device for the sorbent. As mentioned in discussing the previous subsystem, air from injection blower B-102 can also be supplied with limestone directly from the pulverizing system for direct injection of sorbent. The storage and conveying equipment is designed to provide flexibility with regard to sorbent type and source. A separate fill line on silo S-102 allows hydrated lime or prepulverized limestone to be received from hopper trucks. The silo will accommodate approximately 2.5 days' supply of hydrated lime and 3 days' supply of pulverized limestone at the design feed rates.

Furnace Sorbent Injection. This subsystem consists of the equipment required to distribute the pneumatically conveyed sorbent to three boiler levels and to multiple injection points at each level, and to accomplish the injection of the sorbent into the boiler to achieve complete mixing in the flue gas stream. This is a critical area of the design in terms of the process fundamentals. The choice of injection location, for example, largely determines the residence time and temperature history that the sorbent experiences in the furnace. Injection location combined with injection nozzle design and sorbent transport air rates may also have a major impact on the extent and rapidity of sorbent-flue gas mixing in the furnace. The general arrangement of the injection system in shown in Figure 3. A central injection header feeds the three injection levels. The injection header is supplied directly by the sorbent injection blower, B-102. Only one injection level is in use for a given test. Manually operated gate valves are used to isolate the remaining levels. Each injection level has four injection ports which penetrate the boiler wall. The air-sorbent stream from the main header is split using an available impact splitting technology. The nozzle sizes and solids/air ratio for the injection system are based on preliminary jet penetration calculations. It was found that sufficient jet penetration could be achieved with four 2.5-inch nozzles and a total air flow of 2,000 scfm (500 scfm per nozzle). However, the importance of mixing requires that a detailed analysis of sorbent injection be undertaken prior to a detailed process design. Work is currently under way on this topic within the EPRI/SCS program.

Trona Handling and Injection. The trona injection subsystem provides for the receiving, storage, and injection of prepulverized trona in the 25-percent slipstream ahead of the pilot baghouse. In the Plant Scholz conceptual design, the trona--which consists primarily of sodium bicarbonate and sodium carbonate in a hydrated mixture--is assumed to be available in a prepulverized form. The pulverized trona is received in hopper trucks and is loaded into a 7-day storage silo (S-105). The trona injection stream is discharged from the silo to a weigh-belt feeder which meters the sorbent into the injection line. A blower (B-105) provides up to 115 scfm of air for injection into the baghouse slipstream. The equipment for this subsystem is similar to that used for limestone storage and conveying. However, information from a commercial supplier of trona indicates that testing of the handling properties of the material should be undertaken before final design.

Solid Waste Handling and Disposal. The waste handling subsystem is designed to remove solids from the economizer, air heater, precipitator, and baghouse ash hoppers on a continuous basis via a conventional vacuum conveying system. The waste is conveyed to a covered storage silo (S-106) providing 2 days' storage at the process design point. The cementitious nature of the material dictates that a certain amount of storage be provided in order to avoid having to place the material in the landfill during prolonged periods of heavy rainfall and to prevent the waste processing equipment from being critical to daily process operation. From the silo, the waste is metered into a pugmill in which it is mixed with water. A water addition rate of 28 percent by weight of the waste solids flow is assumed in this study based on laboratory tests of ash collected during DSEC pilot work. The mixed effluent from the pugmill fills a dump truck. Two trucks alternate hauling and filling cycles to allow continuous waste processing in the pugmill.

As indicated previously, a dry landfill disposal system has been selected for purposes of the conceptual design in order to minimize site impact and test the landfill disposal concept. The assumed arrangement of the landfill areas is shown in Figure 4. As the figure indicates, separate landfill areas have been designated for sodium containing waste and waste without sodium. The drawing also gives details of the runoff ditch system, holding pond, pumping system, and monitoring wells as well as showing a section through the landfill area. Note that lining of the landfill areas is not included in this study because of the expected stability and low permeability of the compacted DSEC waste. Major design assumptions are noted on the drawing.

Central Instrumentation and Controls. Instrumentation and control requirements have been addressed specifically to ensure that their effect on cost is not neglected. Major measurements required for the prototype program include gaseous species concentrations, continuous coal flow rate, continuous sorbent flow rate, total air flow rate, and various air and flue gas temperatures and pressures to monitor unit operation. The large number of data inputs to be monitored can best be handled by a computerized data logging and recording system to facilitate real-time data collection and processing. An extractive flue gas sampling system is included in the process design to provide critical information on process efficiency and supply data for process control. Accurate coal flow rates are obtained by modifying existing coal feeders to yield continuous gravimetric outputs. Weigh-belt feeders are used to provide continuous sorbent flow rates. The centralized control functions for the process are handled by a programmable controller with an active mimic panel. This equipment is a microprocessor-based system that provides for manual or automated control of all equipment. It is more compact, more versatile, and less expensive than a relay-based control system. A duplicate active mimic panel will be installed in the plant control room.

Miscellaneous and Shared Facilities. This subsystem was included as a "catch-all" to account for equipment shared by multiple process areas. Examples include main transformers, process area lighting and communications, and a process area sump.

Unit Modifications. This subsystem consists of two modifications to the existing unit: a precipitator flue gas conditioning system and an upgrade of the existing boiler sootblower system. Pilot tests at Southern Research Institute indicate that the resistivity of DSEC flyash may increase by up to two orders of magnitude during dry sorbent injection. The high flyash resistivity may lead to degraded precipitator efficiency at the same time that the precipitator inlet grain loading is doubled or even tripled by sorbent injection. For the DSEC prototype design, it has been assumed that flue gas conditioning with SO_3 will be necessary to maintain compliance with particulate emissions standards. The type of system recommended in this study is a liquid SO_2 conversion system. To minimize capital costs, it is assumed that the main components of the system--the vaporizer and converter--will be rented. The rest of the system consists of an injection system, electrical wiring and controls, and a rail tank car or other vessel for storage of liquid SO_2. These items are included as capital cost items.

The dry sorbent injection process has the potential to increase furnace wall and convection surface deposits because of the increase in ash loading and potential changes in flyash chemistry. Therefore, an evaluation of the existing sootblowing system at Plant Scholz was undertaken in preparation for the prototype study. Sootblowing capabilities were judged to be adequate in most respects to cope with furnace sorbent injection. Three relatively minor modifications to the existing system are assumed in the study to provide an extra margin of performance: an increase in sootblowing pressures beyond present levels (125 to 175 psi), an increase in sootblowing frequency, and the installation of four additional wallblowers in existing bent-tube openings in the lower furnace. Only the last of these modifications has significant capital costs associated with it.

PROTOTYPE FACILITY CAPITAL AND O&M COSTS

Based on the process design outlined in the preceding sections, a conceptual cost estimate was prepared for a prototype demonstration of the DSEC process at Plant Scholz. The costs addressed in this study consist of a grand total capital cost and operating and maintenance (O&M) costs for the project. Major project costs not addressed include project management, test consultants and subcontractors, system production costs, and site restoration. The assumptions employed in the study are specific to the Plant Scholz site and are not necessarily consistent with generic assumptions recommended by EPRI. The following sections summarize the more important cost assumptions and present the results of the estimate.

Prototype Capital Costs

Capital Cost Assumptions. The components of capital cost employed in the estimate are shown in Table 5. These are the standard components used by SCS in estimating costs for Gulf Power Company. The table indicates how the grand total capital cost is calculated from the components. The indicated percentages are based on SCS cost estimating guidelines and experience. Direct project costs were estimated based on the process flow diagram and design assumptions presented previously. All direct and engineering costs for the project were estimated in April 1, 1984 dollars and were escalated to January 1, 1986 dollars using annual escalation rates of 7 percent for direct costs and 8 percent for engineering costs.

Capital Cost Estimate. The results of the capital cost estimate are shown in Table 6. The total capital cost for the prototype is estimated to be $6.75 million in dollars as of January 1, 1986, which represents a time near the projected midpoint of the design and construction efforts. The table breaks the capital costs down by the process subsystems described in the preceding section. Indirect costs, however, are added to the total direct costs for the project. Several points should be made about the figures presented in Table 6. First, the estimation of engineering costs is based on a maximum of home-office engineering and a minimum of field engineering and field routing by subcontractors. This approach tends to shift some costs from the category of directs (through subcontractor overheads and profits) into the category of engineering, although the total of the two should not change appreciably. Second, the capital cost estimate does not include any charges for operating-company engineering and review, which was difficult to estimate because of the research status of the project. Third, the breakdown of costs by subsystem is somewhat artificial from an engineering standpoint and subsystem costs are expected to have a greater range of error than the total cost estimate. Finally, the costs shown are for a research facility at a small plant and should not be extrapolated to a full-scale production facility.

Prototype O&M Costs

O&M Cost Assumptions. The components of O&M cost are identified as fixed and variable costs in Table 7. The notes to this table provide a brief summary of the basis on which the O&M costs were estimated. However, several points should be emphasized. As indicated in note (7), limestone and hydrated lime costs include shipment by truck approximately 300 miles under the assumption that sorbents from a range of geographic locations will be tested. Sorbent costs could be reduced by specifying locally available limestone and lime. With regard to O&M labor, the staffing specified in this study is assumed to be in addition to the plant staff for budget estimating purposes. No effort was made to examine the use of existing plant personnel to perform process O&M functions. It should also be noted that all labor includes appropriate overheads and profit and is based on union labor rates. Both labor and consumables were priced specifically for a Plant Scholz test and may not be typical of costs at other sites in other regions. Annual escalation rates based on SCS projections range from 5.5 percent for energy to 7 percent for sorbents and chemicals.

O&M Cost Estimate. The estimated O&M costs are tabulated in Table 7. The costs apply to a one-year test in 1987 and are reported in dollars as of July 1, 1987. However, unit costs are given in dollars as of April 1, 1984. The total annual O&M cost of the prototype facility is estimated at $3.25 million.

ALTERNATE PROTOTYPE CONFIGURATIONS

The prototype cost estimate indicates that a facility designed for an extended test of the integrated DSEC concept at Plant Scholz would require some $6.75 million in capital costs and $3.25 million per year in O&M costs. Such a facility clearly represents a major investment of resources which must be evaluated in light of the potential benefits of the test program. To assist in this evaluation, it is worthwhile to consider how prototype costs could be reduced and what information would be lost by such a reduction.

Alternate Plant Scholz Design

Figure 5 shows in schematic form the Plant Scholz design presented in this study along with a lower-cost alternative design to support a reduced-scope test program. The lower-cost design eliminates two major subsystems, viz. on-site limestone pulverization and sodium injection, reducing the capital cost to approximately $5 million. The elimination of on-site pulverization has several implications. First, it means that prepulverized limestone must be purchased for the test program, which will probably increase sorbent costs. Second, it limits flexibility in testing different limestones since many limestones are not available in prepulverized form. Third, it precludes the possibility of evaluating tradeoffs between grinding costs and the effect of limestone grind size on the process. The elimination of sodium injection has the obvious effect of precluding the integrated testing of in-furnace calcium injection and post-furnace sodium injection. On the other hand, post-furnace sodium injection has been tested extensively by EPRI in other programs, and the sodium injection step as specified here contributes relatively little overall SO_2 removal in the DSEC process. An evaluation of O&M costs for the lower-cost test facility was beyond the scope of the prototype cost study. However, a comparison of the costs of raw versus prepulverized limestones purchased for the EPRI/SCS pilot program suggests that savings in O&M costs due to the reduced scope would possibly be offset by the higher cost of the prepulverized product required by the elimination of on-site pulverization.

Generic Prototype Cost Reductions

While the costs associated with the Plant Scholz prototype should not be viewed as generic costs for a prototype facility, they can be used to suggest the most effective ways of reducing costs for prototype DSEC work done elsewhere. An examination of the cost data given in Table 6 indicates that materials handling and processing represent over 50 percent of the prototype capital costs. This suggests the following possible means of cost reduction:

- Select a smaller prototype boiler (e.g., an industrial facility) to reduce the size of the materials handling equipment.
- Select a prototype test site with existing materials handling facilities such as limestone/lime handling equipment or a dry ash disposal system (e.g., a small unit at a site which includes large scrubbed units).

CONCLUSIONS

SCS has used its research and engineering experience along with the results to date of the EPRI/SCS pilot program to conduct a conceptual design and cost study for a DSEC prototype facility at Plant Scholz. The design provides for on-site pulverization of limestone, the receiving and storage of prepared sorbents, injection of calcium-based sorbents at three levels in the upper furnace, the injection of a sodium compound ahead of an existing slipstream baghouse, and the storage, processing, and landfill disposal of the DSEC waste product. The design is characterized by flexibility and similarity to a commercial system. The estimated prototype costs are $6.75 million in capital and $3.25 million in annual operating and maintenance costs for a test program conducted in 1987. Capital costs can be reduced to approximately $5 million by the elimination of on-site limestone pulverization and sodium injection. While the elimination of sodium injection should not significantly affect the program, the elimination of on-site pulverization of limestone will reduce flexibility with respect to limestone supply, complicate the evaluation of grinding costs and limestone particle size effects, and perhaps increase limestone costs.

ACKNOWLEDGMENTS

The author gratefully acknowledges the substantial contributions of SCS design, cost, and research engineers to this study. Appreciation is also extended to the personnel of Gulf Power Company's Plant Scholz for their cooperation in all phases of the DSEC project. Finally, the author wishes to thank representatives of the Electric Power Research Institute, Southern Research Institute, and KVB, Inc., for their input and guidance.

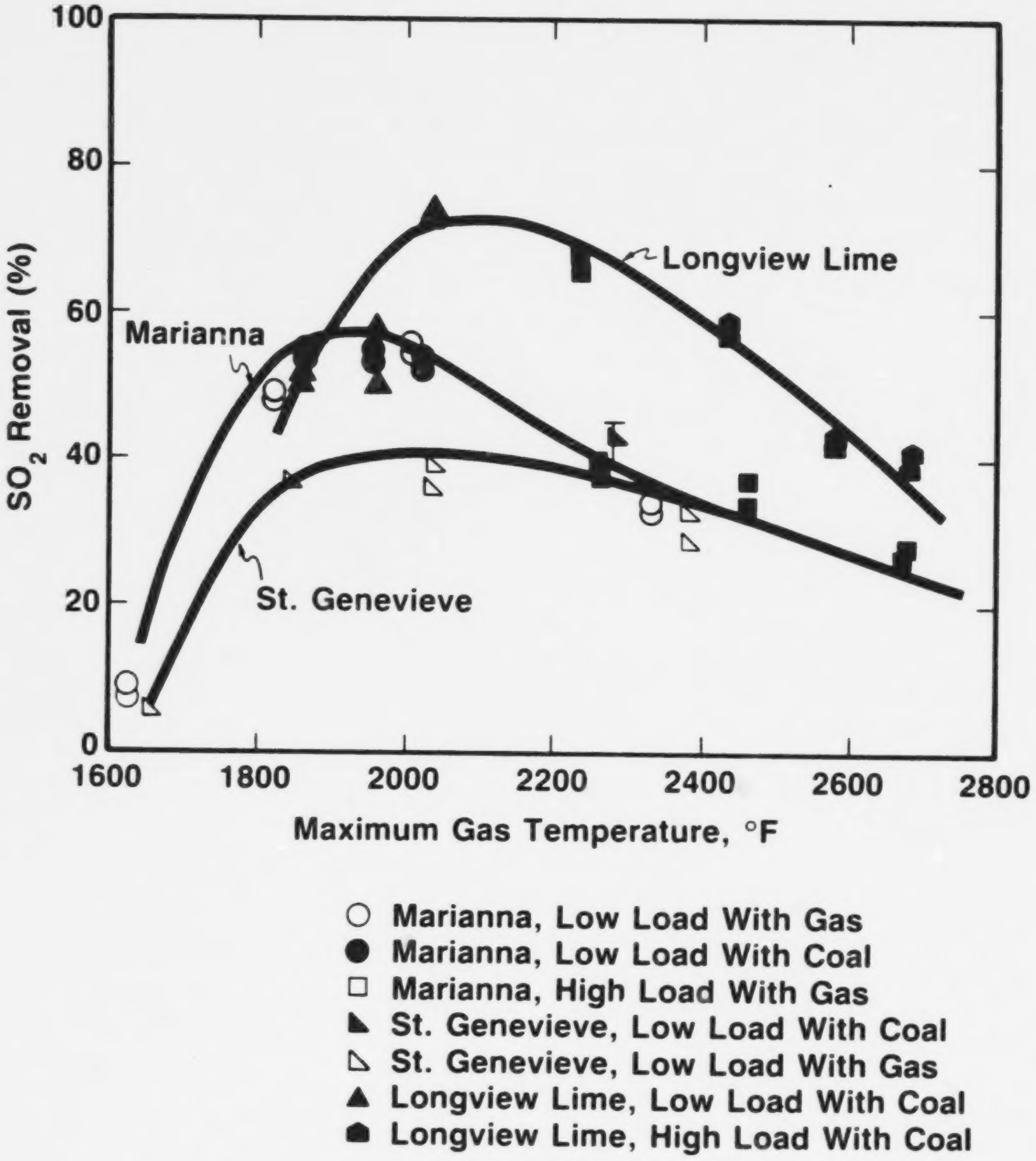

Figure 1. Relationship of observed SO_2 reduction and maximum gas temperature at the point of injection for Marianna and St. Genevieve limestones and Longview hydrated lime tested in Southern Research Institute's research combustor.

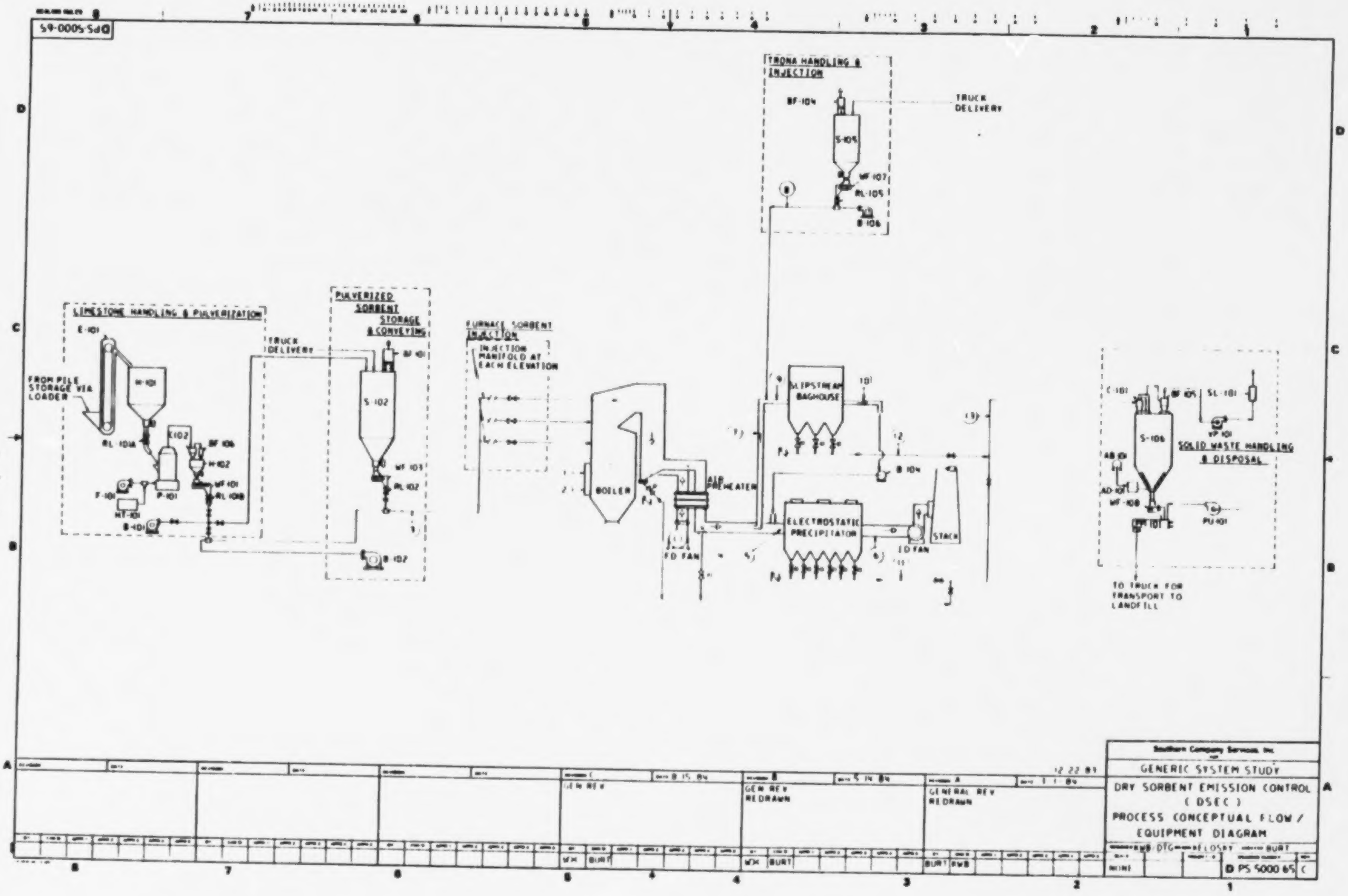
DPS5000-65
LIMESTONE HANDLING & PULVERIZATION
E-101
FROM PILE STORAGE VIA LOADER
H-101
RL-101A
E102
BF 106
H-102
WF 101
RL 108
P-101
F-101
HT-101
B-101
TRUCK DELIVERY
PULVERIZED SORBENT STORAGE & CONVEYING
BF 101
S-102
WF 103
RL 102
B 107
FURNACE SORBENT INJECTION
INJECTION MANIFOLD AT EACH ELEVATION
BOILER
AIR PREHEATER
FD FAN
TRONA HANDLING & INJECTION
BF-104
S-105
WF-107
RL-105
B-106
TRUCK DELIVERY
SLIPSTREAM BAGHOUSE
B 104
ELECTROSTATIC PRECIPITATOR
ID FAN
STACK
C-101
BF 105
SL-101
VP 101
S-106
SOLID WASTE HANDLING & DISPOSAL
AB 101
AD-101
WF-108
PU 101
TO TRUCK FOR TRANSPORT TO LANDFILL
GEN REV
8 15 84
GEN REV REDRAWN
5 14 84
GENERAL REV REDRAWN
1 1 84
12 22 83
WJH
BURT
RWB
Southern Company Services, Inc.
GENERIC SYSTEM STUDY
DRY SORBENT EMISSION CONTROL (DSEC)
PROCESS CONCEPTUAL FLOW / EQUIPMENT DIAGRAM
RWB DTG FELOSKY BURT
NONE
D PS 5000 65
C

Figure 2. Dry Sorbent Emission Control Prototype Process Flow/Equipment Diagram

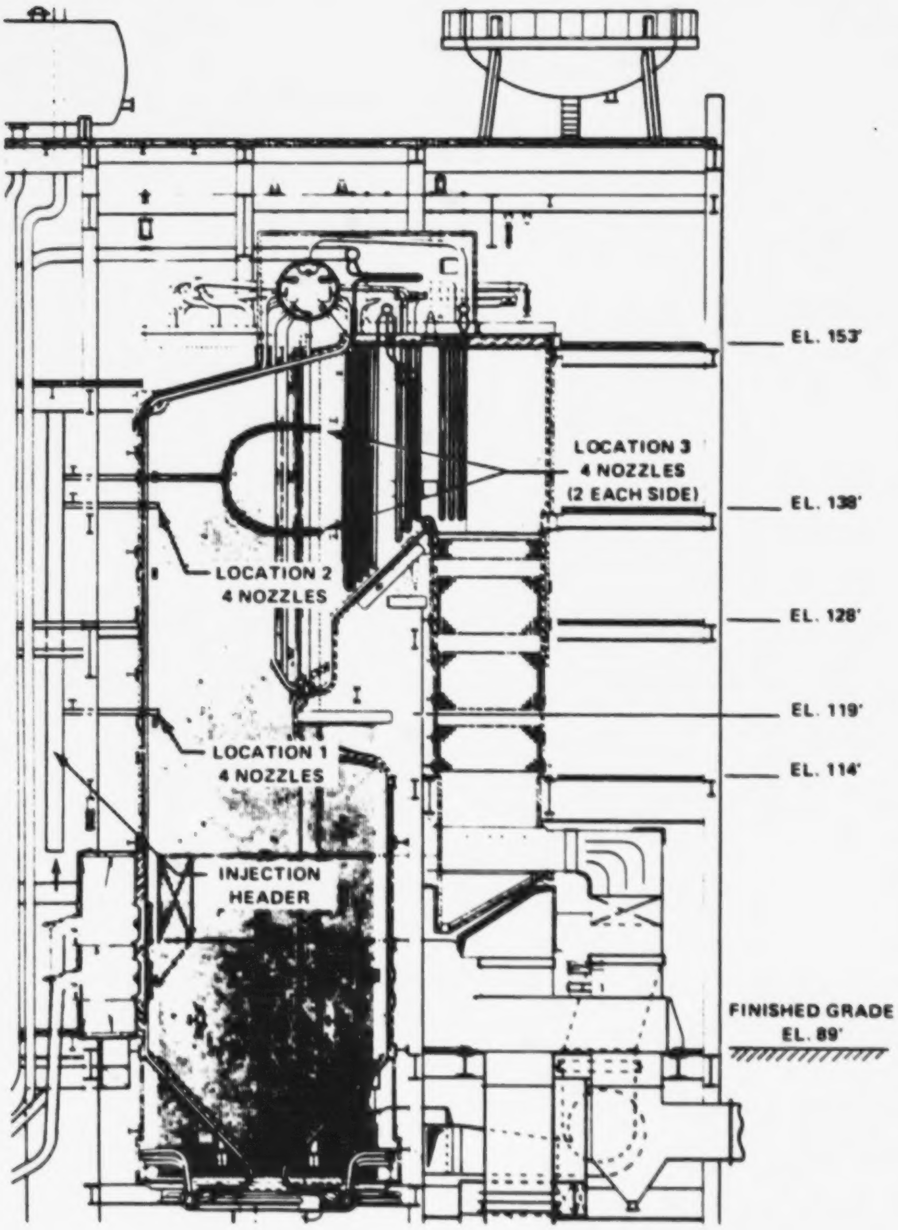
EL. 153'
LOCATION 3
4 NOZZLES
(2 EACH SIDE)
EL. 138'
LOCATION 2
4 NOZZLES
EL. 128'
EL. 119'
LOCATION 1
4 NOZZLES
EL. 114'
INJECTION
HEADER
FINISHED GRADE
EL. 89'

Figure 3. Location of sorbent injection levels in Plant Scholz boiler.

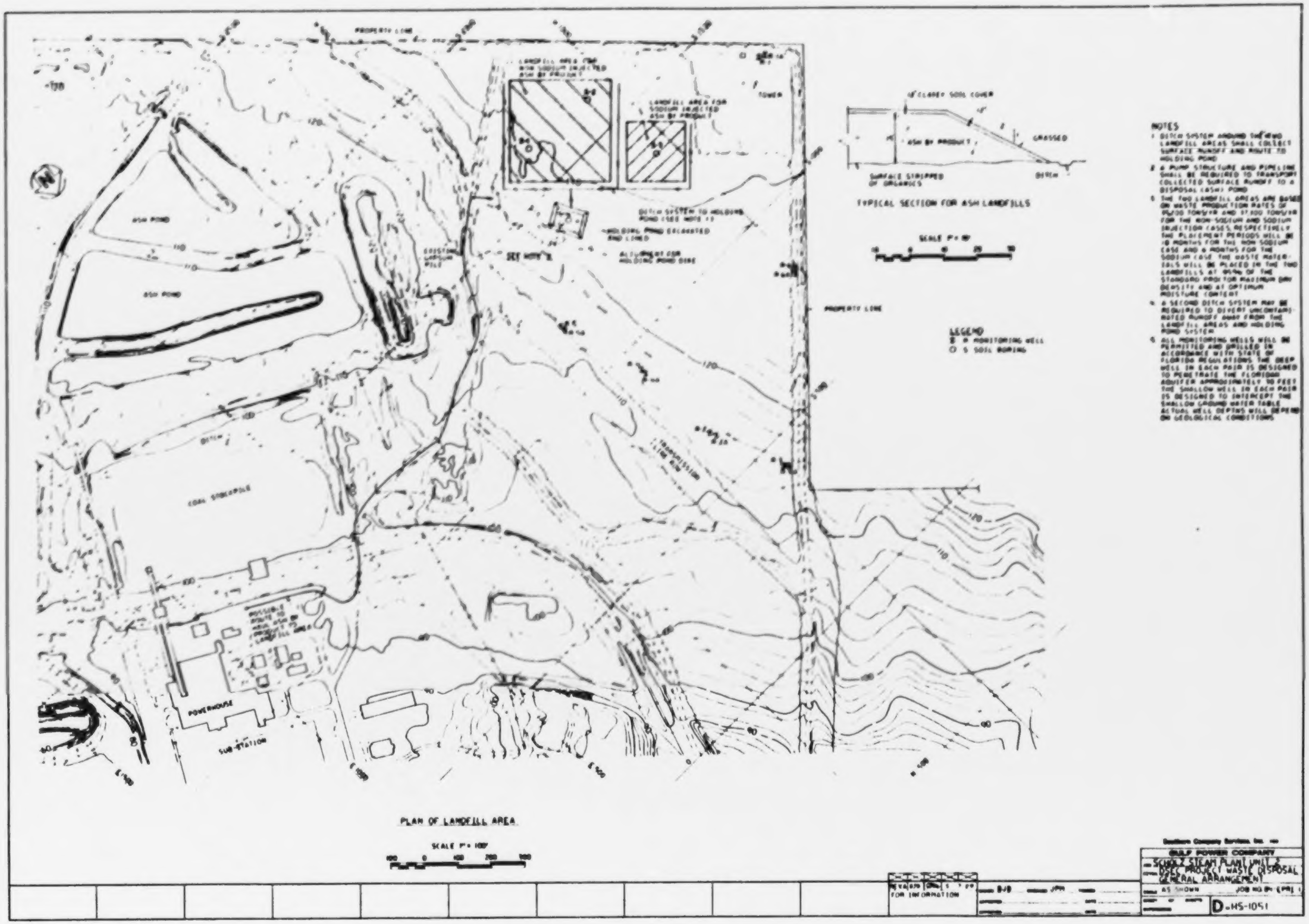
PROPERTY LINE
ASH POND
ASH POND
COAL STOCKPILE
POWERHOUSE
SUB-STATION
TRANSMISSION LINE R/W
SEE NOTE 2
LANDFILL AREA FOR SODIUM INJECTED ASH BY PRODUCT
DITCH SYSTEM TO HOLDING POND (SEE NOTE 1)
HOLDING POND EXCAVATED AND LINED
ALLOTMENT FOR HOLDING POND DIKE
TOWER
PROPERTY LINE
12" CLAYEY SOIL COVER
ASH BY PRODUCT
GRASSED
SURFACE STRIPPED OF ORGANICS
DITCH
TYPICAL SECTION FOR ASH LANDFILLS
SCALE 1" = 10'
LEGEND
M MONITORING WELL
S SOIL BORING
NOTES
PLAN OF LANDFILL AREA
SCALE 1" = 100'
Southern Company Services, Inc.
GULF POWER COMPANY
SCHOLZ STEAM PLANT UNIT 2
DSEC PROJECT WASTE DISPOSAL
GENERAL ARRANGEMENT
AS SHOWN
FOR INFORMATION
D-HS-1051

Figure 4. Conceptual design and arrangement of DSEC waste disposal areas.

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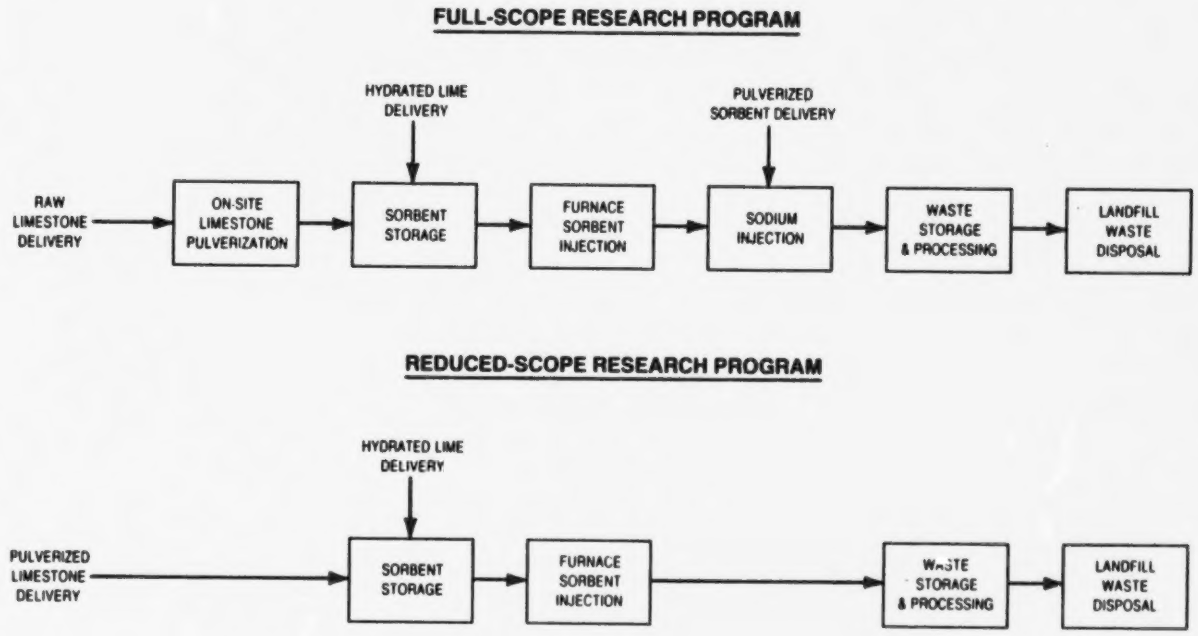
FULL-SCOPE RESEARCH PROGRAM
RAW LIMESTONE DELIVERY
ON-SITE LIMESTONE PULVERIZATION
HYDRATED LIME DELIVERY
SORBENT STORAGE
FURNACE SORBENT INJECTION
PULVERIZED SORBENT DELIVERY
SODIUM INJECTION
WASTE STORAGE & PROCESSING
LANDFILL WASTE DISPOSAL
REDUCED-SCOPE RESEARCH PROGRAM
PULVERIZED LIMESTONE DELIVERY
HYDRATED LIME DELIVERY
SORBENT STORAGE
FURNACE SORBENT INJECTION
WASTE STORAGE & PROCESSING
LANDFILL WASTE DISPOSAL

Figure 5. Diagram of two scope options for a DSEC prototype research program at Plant Scholz.

Table 1
DSEC Major Design Criteria

Boiler Performance Criteria

Design Output (Gross)	40,000 kW
Heat Rate (Gross)	11,000 Btu/kWh
Excess Air (Economizer Exit)	30%
Coal Sulfur Converted to SO_x	100%
Top/Bottom Ash Split:	
Coal Ash	85%/15%
Injected Sorbent	100%/0%

Coal Analysis

Moisture	5.5%
Ash	12.0%
Sulfur	3.5%
Volatile Matter	35.0%
Carbon	68.0%
Hydrogen	4.0%
Nitrogen	1.0%
Oxygen	6.0%
Coal heating value	12,000 Btu/lb

Sorbent Analysis, % by wt.

Sorbent	$CaCO_3$ or $Ca(OH)_2$	$MgCO_3$ or $Mg(OH)_2$	Na. Sesq.(1)	Inerts
Limestone	90	5	--	5
Hydrated Lime	94	2	--	4
Trona	--	--	90	10

Sorbent Stoichiometries and Removal Efficiencies(2)

Sorbent	Location	Molar Ratio	ΔSO_2	Removal Basis
Limestone	Furnace	Ca/S = 3	60%	Uncontrolled emissions
Hydrated Lime	Furnace	Ca/S = 2	60%	Uncontrolled emissions
Trona	Slipstream	Na/S = 3	60%	SO_2 at point of injection
Unreacted Lime	Baghouse	(3)	25%	SO_2 at baghouse inlet

(1) Sodium sesquicarbonate: $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$.

(2) Removals shown are assumed for equipment sizing and do not necessarily represent the potential of the technology.

(3) Removal occurs on the baghouse filter cake due to unreacted CaO carried over from furnace limestone injection at Ca/S = 3. When trona is being injected, combined slipstream SO_2 removal by sodium and unreacted calcium is assumed to be 70 percent based on slipstream inlet SO_2.

TABLE 2

Process Operating Basis and Storage Capacities(1)

Equipment Operating Basis	Shifts/Day	Days/Week
Front-end loader (raw limestone to bucket elevator E-101)	1	7
Limestone pulverizer (P-101)	3	7
Pugmill (PM-101)	1	7
Solid waste landfill mobile equipment	1	7

Equipment Storage Capacities(2)	
Raw limestone stockpile	30 days
Limestone receiving hopper (H-101)	20 hours
Pulverizer product hopper (H-102)	30 minutes
Pulverized limestone silo (S-102)	3 days
Solid waste storage silo (S-106)	2 days
Pulverized trona silo (S-105)	7 days

Capacities of Waste Landfill Areas(3)	
Non-sodium waste disposal area	18 months
Sodium containing waste disposal area	6 months

(1) Equipment numbers refer to process flow diagram (Figure 2).

(2) All equipment capacities at the process design point as defined by the criteria in Table 1.

(3) Landfill capacities are based on 60 percent of the process design point for a period of 2 years.

TABLE 3
Identification of Major Equipment Items in DSEC Process Flow Diagram

Limestone Handling and Pulverization

E-101	Bucket elevator, 30 TPH, 60-ft. height
H-101	Covered raw limestone hopper, 150-ton capacity, live bin bottom
RL-101A	Rotary airlock feeder
P-101	Roller-and-race limestone pulverizer with internal rotary classifier, 10 TPH of product @ 90%-325 mesh and 2-percent moisture, variable speed drive
F-101	Main pulverizer fan
HT-101	Oil-fired pulverizer heater
C-102	Pulverizer cyclone collector
BF-106	Bag filter for secondary limestone collection
H-102	Pulverized limestone feed hopper, 2.5-ton capacity, with bin activator
WF-101	Gravimetric weigh-belt feeder, 24-in. belt
RL-101B	Rotary airlock feeder
B-101	Silo loading blower, centrifugal type, 650 scfm, 6 psig

Pulverized Sorbent Storage and Conveying

S-102, BF-101	Pulverized sorbent silo with separation equipment, live bin bottom, and truck fill line, 500-ton capacity (limestone), 10,500 cu. ft.
B-102	Sorbent conveying and injection blower, centrifugal type, 2000 scfm, 4 psig
WF-103	Weigh-belt feeder, 24-in. belt
RL-102	Rotary airlock feeder

Trona Handling and Injection

S-105, BF-104	Pulverized trona storage silo with separation equipment, live bottom, and truck fill line, 85-ton capacity, 6000 cu. ft.
WF-107	Weigh-belt feeder
RL-105	Rotary airlock feeder
B-106	Trona injection blower, centrifugal type, 115 scfm, 3 psig

Solid Waste Handling & Disposal

S-106, C-101, BF-105	Ash storage silo with separation equipment, live bin bottom, 350-ton capacity, 12,000 cu. ft.
VP-101, SL-101	Vacuum pump (1200 acfm @ 16 in. Hg suction) with silencer
WF-108	Weigh-belt feeder
PM-101, PU-101	Pugmill (50 TPH) with water supply pump
AB-101	Aeration blower, 250 scfm, 30 psig
AD-101	Aeration air dryer, dual tower dessicant type

TABLE 4
DSEC Prototype Conceptual Design Material Balance
Limestone and Trona Injection

(All quantities in 10^3 lb/hr)

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Coal	36.7	-	-	-	-	-	-	-	-	-	-	-	-
SO_2	2.56(1)	-	-	1.02	0.84	0.84	0.26	-	0.26	0.08	-	-	-
Air	-	428	9.6	-	-	-	-	0.56	-	-	-	-	-
Flue Gas	-	-	-	520	521	521	130	-	131	131	-	-	-
$CaCO_3$	-	-	12.1	-	-	-	-	-	-	-	-	-	-
CaO	-	-	-	5.4	4.0	-	1.36	-	1.36	-	4.0	1.34	5.3
$CaSO_4$	-	-	-	3.3	2.5	-	0.82	-	0.82	-	2.5	0.87	3.4
Na Sesquicarbonate(2)	-	-	-	-	-	-	-	0.91	-	-	-	-	-
Na_2CO_3	-	-	-	-	-	-	-	-	0.64	-	-	0.39	0.4
Na_2SO_4	-	-	-	-	-	-	-	-	-	-	-	0.34	0.3
Flyash	-	-	-	3.7	2.8	-	0.94	-	0.94	-	2.8	0.94	3.7
Sorbent Inerts	-	-	1.3	1.0	0.8	-	0.25	0.10	0.35	-	0.8	0.35	1.2
Total Solids	36.7	-	13.4	13.4	10.1	(3)	3.37	1.01	4.11	(4)	10.1	4.23	14.3

(1) Uncontrolled SO_2 flow rate in furnace based on 100-percent conversion of coal sulfur.
(2) Sodium sesquicarbonate ($Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O$), the major constituent of trona.
(3) Total particulate flow estimted at 50 lb/hr.
(4) Total particulate flow estimated at 16 lb/hr.

Table 5
Components of Capital Cost

Direct Cost(1)	A
Indirect Charges	
Temporary Construction(2)	B=2%xA
SCS Engineering(3)	C
Field Supervision	D=3%xA
SUBTOTAL	E
General Overhead	F=1%xE
SUBTOTAL	G
Interest During Construction (AFUDC)	N/A(4)
SUBTOTAL	H
Contingency(5)	I=25%xH
GRAND TOTAL, CAPITAL COST	J=A+B+C+D+F+I

(1) Total of base costs of labor, material, and equipment including 3 percent freight and 4 percent sales tax. Direct erection or labor costs include a contractor overhead and profit of 45 percent.

(2) Project costs not chargeable to a direct account, e.g. construction equipment, temporary buildings, safety and security, etc.

(3) Based on engineering manhour estimate and an average burdened manhour rate for SCS. Includes design engineering and project support.

(4) Not applied to this estimate. The research status of this project may dictate special financing considerations which could not be evaluated within the scope of this study.

(5) Consists of scope omission and error contingency of 15 percent and pricing contingency of 10 percent. No allowance has been made for unforseen scope changes.

Table 6
DSEC Capital Cost Estimate
Prototype Demonstration at Plant Scholz in 1987

Costs in 1-1-86 $\$ \times 10^3$

ITEMIZED COSTS:

Subsystem	Materials	Erection	Subcontract	Total Direct Costs	Engineering
Limestone Handling & Pulverization	741.4	156.4	84.4	982.2	149.5
Pulverized Sorbent Storage & Conveying	253.1	105.8	--	358.9	151.8
Furnace Sorbent Injection	--	--	109.2	109.2	8.0
Trona Handling & Injection	95.8	40.0	--	135.8	21.3
Solid Waste Disposal					
In-Plant Handling	670.4	181.7	--	852.1	223.0
Landfill	75.8	32.4	156.0	264.2	118.2
Central Instrumentation & Controls	346.5	298.4	171.8	816.7	130.3
Miscellaneous and Shared Facilities	265.1	88.8	0.1	354.0	149.3
Unit Modifications					
Flue Gas Conditioning	--	--	246.5	246.5	21.6
Sootblower Modifications	27.9	10.2	--	38.1	8.0
TOTALS	2476.0	913.7	768.0	4157.7	981.0

TOTAL COST:

Direct Cost	4157.7
Engineering	981.0
Temporary Construction and Field Supervision	207.9
General Overhead	53.5
Contingency (25%)	1350.0
GRAND TOTAL, CAPITAL COST	6750.1

Table 7
One-Year O&M Costs for DSEC Prototype Test
(1987 Test Year)

	Quantity	Unit Cost $ (4-1-84)	Total Cost $10^3$$ (7-1-87)
Fixed O&M Costs			
Operating labor(1)	26,880 hr	21.75	706.5
Maintenance labor - routine(2)	5,760 hr	18.40	128.1
Maintenance labor - start-up(3)	1,280 hr	19.20	29.7
Maintenance materials(4)	--	--	192.2
Leased equipment			
Flue gas conditioning(5)	--	--	143.9
Mobile equipment(6)	--	--	226.1
	TOTAL FIXED O&M		1426.5
Variable O&M Costs			
Sorbents(7)			
Limestone	30,000 ton	22.00	822.3
Hydrated lime	4,500 ton	70.67	396.2
Trona	750 ton	250.00	225.0
Energy(8)			
Electric power	$4.2x10^6$ kWh	0.045	224.9
#2 fuel oil	10,000 MBtu	6.35	75.6
Diesel fuel	24,350 gal	1.10	31.9
Liquid SO_2(9)	165 ton	250.00	51.4
	TOTAL VARIABLE O&M		1827.3
	TOTAL O&M		3253.8

(1) Consists of 8 process operators (2 operators on shift at all times), and 6 equipment operators to operate limestone and waste handling equipment (4 per shift, 7 days per week).

(2) One I&C technician, one mechanical maintenance worker, and one general laborer on one-shift, 5-day-per-week coverage.

(3) One I&C technician, 2 mechanical maintenance workers, and one general laborer on day shift during first 8 weeks of the program.

(4) Based on maintenance labor/materials cost ratio of 40/60 (routine maintenance labor as base).

(5) Based on estimated $10,000/month for skid-mounted vaporizer and converter escalated to 7-1-87.

(6) Consists of one 2-cu.-yd. front-end loader, one bulldozer (equivalent to Caterpillar D-3), one tractor and sheep's foot roller, and two 12-cu.-yd. dump trucks.

(7) Delivered costs to Plant Scholz. Limestone and hydrated lime costs include shipment by truck approximately 300 miles. Costs of locally acquired limstone and lime would be lower. Trona cost is for a prepulverized product originating in Wyoming and is speculative at this time.

(8) Consists of electricity for process equipment, fuel oil for limestone drying, and diesel fuel for limestone and waste handling mobile equipment.

(9) Liquid SO_2 is for flue gas conditioning. Concentration of 50 ppm SO_3 is assumed because conditioning effectiveness with sorbent injection is not known.

EPA's LIMB COST MODEL: DEVELOPMENT AND COMPARATIVE CASE STUDIES

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Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

ABSTRACT

The LIMB cost model is used to project the capital and annualized costs and the cost per unit of pollutant controlled for LIMB systems installed on generic coal-fired utility boilers. The type of sorbent, unit size, unit life, level of control, and coal sulfur content are among several items specified by the user. In addition, flexibility in user input or default values enables various parametric and sensitivity analyses. Basic economic premises for the model are taken from the EPRI Technical Assessment Guide (TAG™).

Case studies compare various LIMB process options with each other and with wet limestone slurry scrubbing, the current standard SO_x control technology, under a variety of conditions. For a new 500 MW unit burning 1.92% S coal and achieving control to meet NSPS, costs per ton** of sulfur removed are estimated to be $1377 and $1078 for limestone FGD and LIMB using dolomitic hydrate, respectively. At 0.48% S in the coal, these costs are estimated at $3715 and $1366 for limestone FGD and LIMB, respectively. Case studies involving comparisons between LIMB and FGD are accomplished through the use of the LIMB cost model and the TVA Shawnee Flue Gas Desulfurization Computer Model.

INTRODUCTION

EPA's LIMB cost modeling activities are a response to a need for making rapid and accurate comparative economic assessments of LIMB technology with other SO_2 control approaches such as flue gas desulfurization (FGD). This work was initiated in May 1984 with the development of the LIMB cost model described in this paper. Our ability to conduct comparative economic studies has subsequently been augmented by incorporation of cost models for FGD and integrated air pollution control systems that were developed under earlier EPA contracts. A broad base of cost data for NO_x, SO_x, and particulates resides within EPA's

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* Presenter

** For those more familiar with metric units, see conversions at the end of paper.

Industrial Environmental Research Laboratory at Research Triangle Park. However, the coordination and synthesis of this data base relative to comparative economic assessments are assigned to the LIMB Applications Branch of the Engineering Applications Division of IERL-RTP.

To date, many benefits have derived from EPA's cost modeling work. Among these are:

1. Responsive capability to perform parametric cost sensitivity studies for a broad range of process variables.
2. An ability to make direct comparison, under equivalent premises, of LIMB to other SO_2 control options, particularly FGD.
3. An ability to economically optimize choice of sorbents, calcium-to-sulfur ratios, and SO_2 control levels.
4. Quick response to industrial inquiries where site-specific requirements can be defined.
5. Evaluation and/or reconciliation of cost estimates prepared by other agencies themselves or through Agency-sponsored contracts.
6. Program guidance relative to the focus of research and development efforts as LIMB technology matures.

This paper presents some of the background and illustrative examples resulting from our cost modeling activities.

COMPARISON OF LIMB AND FGD COST ESTIMATING METHODOLOGIES

Process economics like most other quantifiable items is relative; the numbers mean very little in an absolute sense but are very meaningful when they are used to compare two or more processes with each other. Since wet FGD processes are currently the predominant SO_2 controls used for fossil-fueled utility boilers, comparisons between projected LIMB costs and FGD costs were deemed appropriate to investigate the potential economic viability of LIMB. Comparison of LIMB and FGD costs should be done with proper perspective. Since FGD is a relatively mature technology, the projected costs are backed by actual full scale applications experience, whereas LIMB is a relatively new technology and its projected costs are based on pilot data. The accuracy of the FGD costs is expected to be in the range -15%, +30%; accuracy of the LIMB costs is expected to be somewhat less.

The EPA LIMB cost model was developed in-house at the Industrial Environmental Research Laboratory at Research Triangle Park, N.C. (IERL-RTP). The computer program was developed using BASIC language on a Zenith 100 microcomputer. The program and imbedded comments contain approximately 1000 lines of code and, when the optional printed reports are produced, a typical session and associated case study takes less than 3 minutes to complete.

The program is designed for minimum user input of LIMB system operating and performance data and generates corresponding material balances, solids distribution, emissions summary, tons/year SO_2 removed at given capacity factor, detailed capital requirement, operating and maintenance costs, first year costs, levelized costs, and cost per ton SO_2 removed.

The cost model was designed to optimize speed and ease of use by containing "default" economic assumptions and values. These economic values are presented to the user during the session for acceptance as presented, or the user has the flexibility at any time to override the default value and enter his own values.

The cost model was developed as an analytical tool to support parametric sensitivity studies and comparative technology cost studies. The model accepts LIMB performance data and generates associated costs.

Since EPA's LIMB cost model was developed with a high degree of flexibility, an FGD model with a similar degree of flexibility was sought for comparative studies. Fortunately, TVA developed just such a model called the Computerized Shawnee Lime/Limestone (L/LS) Scrubbing Model under an interagency agreement with EPA. This model accepts about 150 user input variables and about 20 print control variables and is considered a preliminary design and cost model for wet lime and limestone FGD processes.

Some of the more important numerical values supplied by the user are given in Table 1.

Some of the important options available to the user of the TVA Shawnee L/LS model are shown in Table 2.

The TVA program is a design and cost model for new FGD control systems. To project costs of retrofit systems, a program was written for a TI-59 hand-held calculator to use the results of the TVA program to project the cost of retrofit systems. The basic assumption used was that the total capital investment would increase by 30 percent over that for a new system. The program calculates revised annualized costs by increasing total capital investment and those items that are estimated as a function of capital, but keeps constant items such as labor and unit costs which are not dependent on total capital investment. The FGD retrofit results are based on this program.

COMPARATIVE COSTS OF SO_2 CONTROL TECHNOLOGIES

LIMB technology offers economic advantages over conventional wet FGD methods when moderate SO_2 control levels (45 to 65%) are required. The costs of these SO_2 control technologies have recently been evaluated in considerable detail by EPA based on work conducted by TVA (1); Combustion Engineering, Inc. (2); PEDCo Environmental, Inc. (3), and in-house cost analysis work performed by IERL-RTP.

Since the SO_2 removal efficiencies are different for LIMB and FGD, cost comparisons are presented on a normalized basis; i.e., cost per ton of SO_2 removal. The cost analysis procedures are based to the maximum extent possible on guidelines suggested by the Electric Power Research Institute (4). The current dollar analysis method is used with costs expressed in 1985 dollars. For retrofit units, 15-year levelized costs are used; whereas, 30-year levelized costs are used for new units. Internally consistent costs and/or factors for such items as operating and maintenance labor, maintenance material, administrative and support labor, consumables, and levelization factors have been employed to ensure that the LIMB and FGD costs are on an equivalent basis. Tables 3 and 4 present summaries of the major premises used in the economic analysis. In addition to those shown, there are other indirect charges and assumptions that enter into this rather complex analysis. These include items such as: engineering and home office overhead including fee; project and process contingencies; cost of general facilities; preproduction costs; inventory capital; and land. Some of these charges are based on a percentage of process capital cost, while others are computed based on specific site requirements, cost and quantities of consumables, allowance for funds during construction, etc. It is beyond the scope of this paper to discuss these in any depth, but we have ensured that most charges and assumptions are consistent within and between LIMB and FGD.

Some of the technology-related assumptions used in developing the costs for LIMB are given below:

a. New units are assumed to be already equipped with burners capable of meeting the current NO_2 standard of 0.6 lb/10^6 Btu for bituminous coal and 0.5 lb/10^6 Btu for subbituminous coal.

b. Retrofit units are assumed to be installed with with improved burners capable of meeting NO_2 emissions of 0.7 lb/10^6 Btu.

c. New units are assumed to be already equipped with a bare-tube economizer.

d. Retrofit units are assumed to have an existing finned-tube economizer which is replaced with a bare-tube economizer.

e. Retrofit units have upgraded ESPs to handle the additional solids loading plus SO_3 conditioning to improve resistivity.

f. New units have baghouses which are not charged off as a LIMB-related cost.

g. Both new and retrofit units have sootblower upgrades, a sorbent injection system, and dry waste disposal.

Some of the technology-related assumptions used in developing FGD costs are given below:

a. Spray tower absorbers using limestone slurry and forced oxidation were specified.

b. Waste disposal is by landfill.

c. One spare absorber was specified for new units, and no spares for retrofit cases.

d. Emergency bypass of 50% of the flue gas normally scrubbed is provided.

e. Reheat is by in-line steam tube reheater to 79.4°C (175°F).

For FGD systems, the stoichiometric ratio is defined as the moles of calcium per mole of SO_2 absorbed. For LIMB, the stoichiometric ratio is defined as moles of calcium per mole of sulfur in the fuel. Typically, a stoichiometric ratio of 1.4 is used with FGD for 90% SO_2 control; whereas for LIMB, stoichiometric ratios of 1.4 to 2.5 might be employed depending on the sorbent and required control level. A LIMB system using a Ca/S ratio of 2 and achieving 50 % SO_2 control would be equivalent to a stoichiometric ratio of about 4 using FGD's nomenclature for stoichiometric ratio. The figures in this paper that illustrate the comparative costs of LIMB and FGD use the stoichiometric ratio nomenclature associated with the respective technology. For LIMB, it is shown as Ca/S; for FGD, it is shown as Ca/SO_2.

Table 5 gives the boiler and coal characteristics used for the LIMB and FGD economic analysis. The unit sizes selected represent those typical of retrofit and new applications. Wall-fired designs were used in all cases. The coals encompass the sulfur content range targeted for application of these SO_2 control technologies. The net plant heat rate is used in the analysis to determine the required coal flow and corresponding sulfur and SO_2 mass flow rates.

Table 6 gives the sorbents, Ca/S ratios, and SO_2 control levels used in the LIMB economic analysis. The performance data is derived from pilot scale tests shown in Figure 1 and from in-house testing of sorbents with promoters. Promoted sorbents contain relatively small amounts of mineral substances that are added to enhance the sulfur capture potential of the sorbent. Some very preliminary work conducted to date indicates that the use of a promoter such as sodium carbonate can increase $CaCO_3$ and $Ca(OH)_2$ performance by about 1.4 times that typical of the unpromoted sorbent. The sorbent costs represent delivered costs to the power plant based on current estimates from sorbent suppliers. The selection of these specific Ca/S ratios and corresponding SO_2 control levels resulted from an initial sensitivity and optimization study in which a range of Ca/S ratios and SO_2 control levels were evaluated. The values selected represent the optimum economic levels for these sorbents.

For retrofit units, the Ca/S ratio sets the SO_2 control level. For new units, required SO_2 control levels to meet New Source Performance Standards were determined for the coals being used, which in turn set the Ca/S ratios.

Figure 2 and Table 7 present the results of the economic analysis of LIMB and FGD for retrofits. Note that for intermediate sulfur levels (e.g., 1.92%), LIMB is consistently more cost effective than FGD in the categories of cost per ton of SO_2 removed, total capital requirements, and levelized revenue requirements. For higher sulfur levels (e.g., 3.36%), FGD has a slight edge in terms of cost per ton of SO_2 removed over LIMB when limestone and/or pressure-hydrated dolomitic lime is used as the LIMB sorbent. This is due in part to the scenario chosen for FGD in that FGD would be retrofit to meet NSPS requirements. For FGD, the differential cost in capital requirement and levelized revenue requirement that occurs in going from 1.92 to 3.36% sulfur is offset to an extent by the increased SO_2 control. For LIMB cases, a constant percentage control is assumed for these coals; consequently, on a cost per ton of SO_2 removed basis, LIMB's cost advantage relative to FGD diminishes for limestone or pressure-hydrated dolomitic lime. However, LIMB continues to exhibit an economic advantage when $Ca(OH)_2$ or promoted $Ca(OH)_2$ or promoted $CaCO_3$ is used as the sorbent. Note also, that LIMB consistently showns an advantage over FGD in terms of total capital requirement and is always more than $100/kW cheaper.

Figure 3 and Table 8 present the results of the economic analysis of LIMB and FGD for new units meeting NSPS. Here, LIMB exhibits a significant economic advantage over FGD with the low sulfur coal. With intermediate sulfur levels, LIMB continues to be about 1/3 to nearly 1/2 the cost per ton of SO_2 removed that FGD displays. Table 8 illustrates that for LIMB, the total capital requirement is consistently at least $100/kW less than FGD. For LIMB, the cost per ton of SO_2 removed is affected significantly by sorbent cost as reflected in the line representing the pressure hydrated dolomitic lime. $Ca(OH)_2$, both umpromoted and promoted, appears to be the sorbent of choice for NSPS applications.

An examination of Tables 7 and 8 shows that both processes are O&M intensive, but as a percentage of the total levelized revenue requirements, FGD is slightly less O&M intensive. This results because of FGD's lower sorbent cost and somewhat more favorable sorbent utilization. Despite this, LIMB has overall cost advantages that for many applications appear favorable.

CONTINUING WORK

Comparative Economics

In order to continue economic evaluations of LIMB processes and to evaluate them relative to other competing technologies, plans are underway to modify and update another existing cost and performance model called the Integrated Air Pollution Control System (IAPCS) which was developed by PEDCo Environmental, Inc., under contract with EPA in 1983. The IAPCS was designed to compare the cost and performance of several control technologies used with fossil fueled power plants. Within certain stated limitations, the IAPCS projects the cost and performance of systems consisting of various configurations or combinations of nine control technologies:

- Overfire air/low NO_x burners (OFA/LNB)
- Limestone injection in multistage burners (LIMB)
- Physical coal cleaning (PCC)
- Spray humidification (SH)
- Electrostatic precipitator (ESP)
- Fabric filter (FF)
- Lime spray drying (LSD)

- Flue gas desulfurization (FGD)
- Dry sorbent injection (DSI)

The IAPCS model is currently operational on the IBM mainframe system at the National Computer Center at Research Triangle Park, N.C. The model is interactive--it prompts the user to supply the required input data and to accept or change most of the current numerical parameters.

Currently, it is planned to replace the LIMB, FGD, ESP, and FF modules in the IAPCS with updated versions. The EPA LIMB cost model will be made a part of the IAPCS, replacing the current (i.e., PEDCo) LIMB cost module of the model.

The ESP and FF modules will be replaced by programs developed by Viner and Ensor (5) of Research Triangle Institute under contract with EPA in 1982-1983. We expect to develop an algorithm for predicting flyash resistivity as a function of ash characteristics and LIMB product solids. This will be used to calculate specific collection area and, thus, project more accurate ESP costs.

The current FGD module in the IAPCS model deals only with wet limestone FGD using a spray tower and forced oxidation. We intend to replace this module with an updated version of the TVA Computerized Shawnee Lime/Limestone Scrubbing Model. This will add a lot of flexibility to consider, for example, lime or limestone, forced or natural oxidation, different waste disposal options, and different scrubber types.

In addition to updating and expanding some of the individual IAPCS modules, general improvements are also planned and listed here:

- Inclusion of EPRI guidelines (TAG™) and cost reporting format to allow the user to specify EPRI or TVA cost and reporting format.
- Inclusion of Marshall and Swift cost indices to allow the capability to produce cost estimates for any time frame.
- Expression of results in cost per unit ($/ton) of pollutant removed.

Recycle of Spent Sorbent

Since LIMB annualized costs and cost per unit pollutant removed are O&M intensive and much of the sorbent remains unused, the potential exists to reduce costs by recycling some of the unused sorbent in the waste. To do this, a process would have to be designed and installed to enrich the spent sorbent in unused reactant and simultaneously produce a waste product poorer in unused reactant. Such a process would require additional capital investment and operating revenue but would balance this cost with a savings in sorbent cost for the overall LIMB process.

Although the LIMB cost model cannot be used to conceive and design such a process, it can be used to determine break-even costs for the installation and operation of the potential process. The LIMB cost model has been modified to consider recovery and recycle. The user must supply inputs concerning the enrichment of the waste and the percent recycle. The cost model will then be used to help guide a preliminary engineering study of potential recycle schemes, rejecting from further study those not economically viable.

Sensitivity Analysis and By-Product Credit

The model is expected to be used extensively in studying many economic aspects of LIMB processes to help guide the expenditure of resources in basic research and engineering studies so that these resources will be spent where there is the most potential for practical application.

Sensitivity analyses based on the model may be used to examine the effects of such items as by-product credit, sorbent cost, capacity factor, and stoichiometry on the process economics for a range of applications. By-product credit is of particular interest because the LIMB processes will produce greater quantities of waste (dry basis) than the currently used SO_2 control technologies. As more is learned about the LIMB process and its wastes, beneficial utilization techniques will be sought and further developed if economically viable. The LIMB cost model or an upgraded version will be used to focus on the techniques with most economic potential. Sensitivity of the LIMB process with respect to sorbent cost and stoichiometry is an important consideration for reducing operating costs and further improving LIMB's projected cost advantage.

CONVERSION UNITS

To convert from	to	Multiply by
lb/10^6 Btu	ng/J	433
tons	metric tonnes	0.907
Btu	J	1055
lb	kg	0.454
gal.	liters	3.78

REFERENCES

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3. Baker, G., et al., "User's Manual for the Integrated Air Pollution Control System Cost and Performance Program." Draft Final Report for EPA Contract No. 68-02-3693 (3,6), October 1984.

4. Electric Power Research Institute, "Technical Assessment Guide," EPRI P-2410-SR, May 1982.

5. Viner, A. S. and Ensor, D. S., "Computer Programs for Estimating the Cost of Particulate Control Equipment," EPA-600/7-84-054 (NTIS No. PB 84-183573), April 1984.

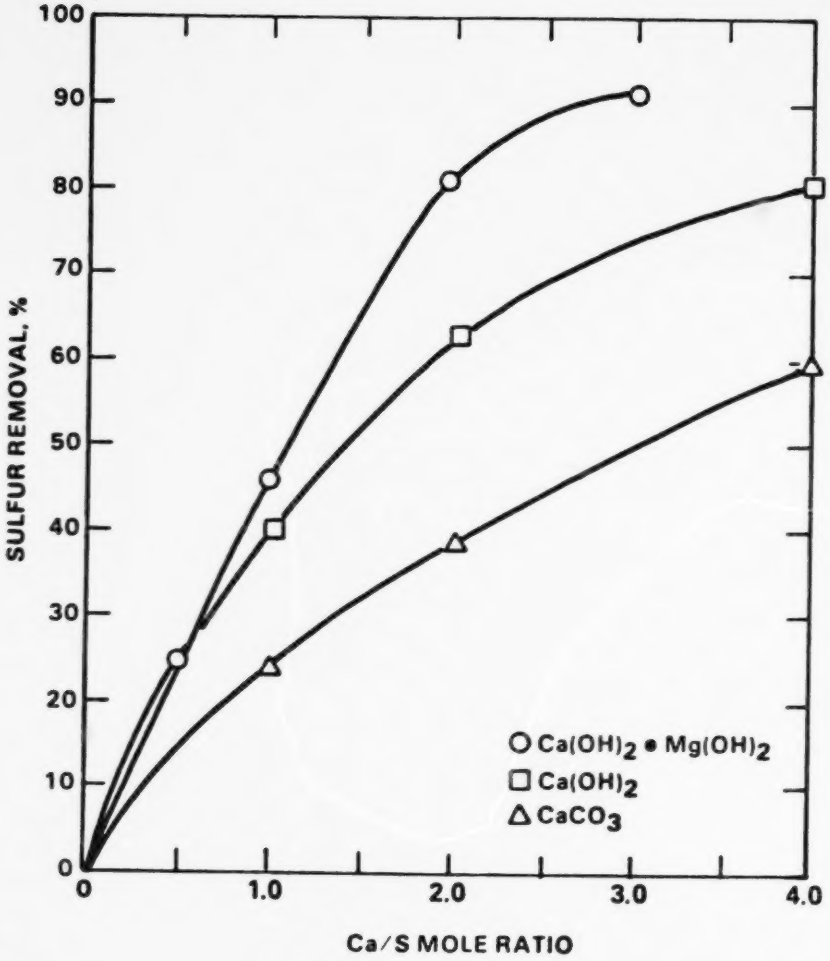

Figure 1. Typical sorbent performance.

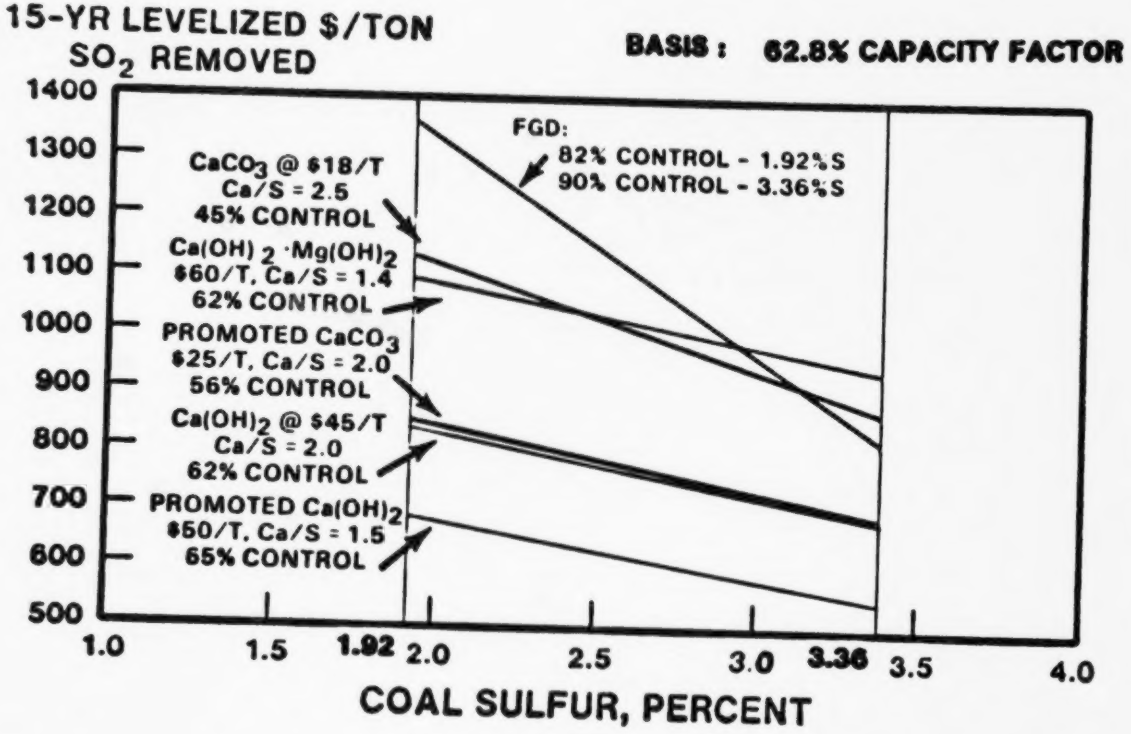

Figure 2. Comparison of SO_2 control technology cost; 300 MWe retrofit.

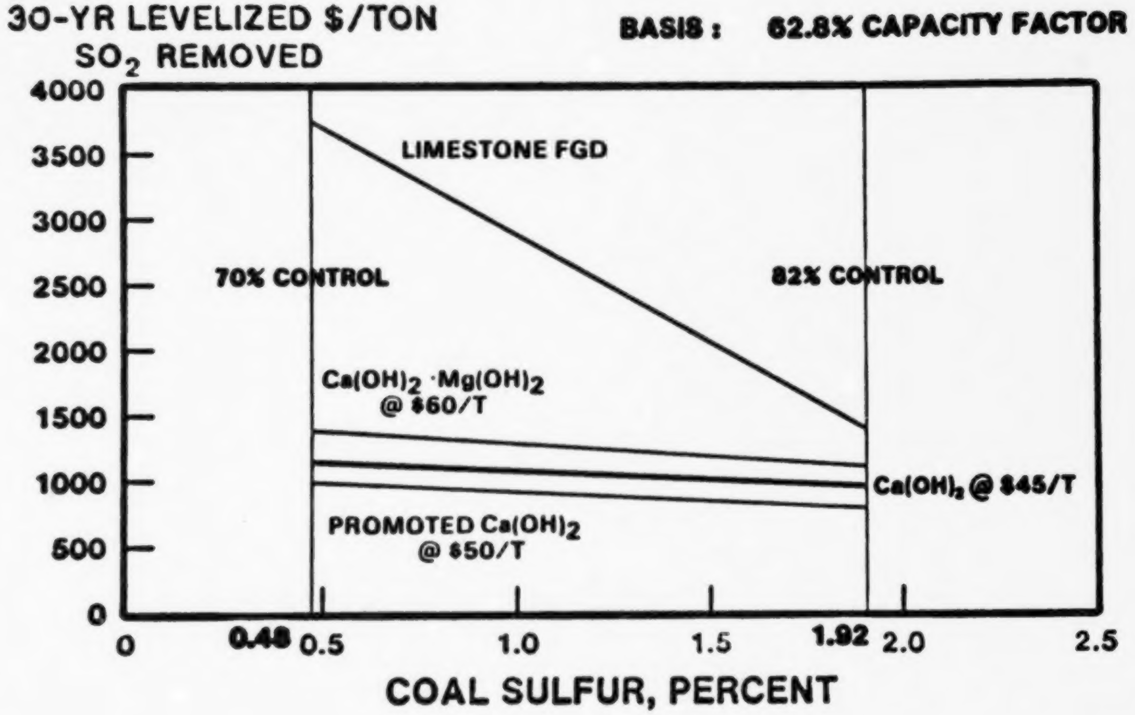

Figure 3. Comparison of SO_2 control technology cost; 500 MWe NSPS.

Table 1

SOME NUMERICAL VARIABLES FOR THE TVA SHAWNEE LIME/LIMESTONE SCRUBBING MODEL

Boiler

- Electric power output
- Boiler heat rate
- Heating value of coal
- Excess air, %
- Temperature of hot gas to scrubber

Coal Composition, wt %, C, H, O, N, S, Cl, Ash, H_2O

Scrubber

- SO_2 removal, %
- Temperature of stack gas
- L/G ratio
- Hold tank residence times
- Superficial gas velocity
- Sorbent stoichiometry
- Oxidation rate
- Air stoichiometry (for forced oxidation)
- Solids in filter cake, %

Waste Disposal

- Sludge disposal fee, $/ton dry sludge
- Land area for pond, acres
- Land cost, $/acre
- Distance from scrubber area to disposal site
- Pond liner cost, $\$/yd^2$

Indirect Costs as percentage of direct construction expense

Economics

- Levelizing factor for O&M
- Levelizing factor for capital charge
- Sales tax
- Freight rate
- Royalties
- Chemical engineering material cost index
- Chemical engineering labor cost index

Unit Costs for limestone, lime, additives (if applicable), labor, utilities

Operating Profile

- Number of years of operation
- Operating hours per year
  (capacity factor = operating hours per year ÷ 8760)

Table 2

SOME IMPORTANT OPTIONS FOR TVA SHAWNEE LIME/LIMESTONE SCRUBBING MODEL

Emergency bypass

Partial scrubbing/bypass

Coal cleaning

Pollutant Removal - % removal, NSPS, $lb/10^6$ Btu

Stoichiometry, L/G, SO_2 removal
(scrubber design based on any two of these three)

Sorbent - lime or limestone

Additives - MgO or adipic acid

Forced Oxidation

Scrubber Type - spray tower, venturi, TCA, and combinations of these

Sludge Disposal - thickener, filter, ponding, lining, fixation, landfill, and combinations of these

Economic Premises

Table 3

MAJOR ECONOMIC PREMISES FOR COST OF CAPITAL

	New Units	Retrofit Unit
Base year for cost comparison	1985	1985
Book life, years	30	15
Tax life, years	15	5
Inflation rate, %/yr	8.5	8.5
Debt/equity ratio	50/50	50/50
Debt cost, %/yr	11.0	11.0
Preferred stock ratio, %	15	15
Preferred stock cost, %/yr	11.5	11.5
Common stock ratio, %	35	35
Common stock cost, %/yr	15.3	15.3
Weighted cost of capital, %/yr	12.5	12.5
Federal plus state income tax rate, %	50	50
Property taxes and insurance, %/yr	2	2
Investment tax credit, %	10	10
Levelized carrying charge rate, %	15.3	16.01

Table 4

MAJOR ECONOMIC PREMISES FOR OPERATING AND MAINTENANCE COSTS

	New Units	Retrofit Units
Base year for cost comparison	1985	1985
Unit capacity factor, %	62.8	62.8
Book life, years	30	15
Tax life, years	15	5
Levelizing factor	2.314	1.714
Waste disposal cost, $/ton	7.66	7.66
Operating manhours/year		
LIMB	43,800	43,800
FGD	55,460	55,460
Average labor rate, $/hr	23.37	23.37
Limestone cost, $/ton[a]	17.88	17.88
Water, $/1000 gal.	0.77	0.77
Process steam, $/1000 lb	4.84	4.84
In-plant power, mills/kWh	58	58
Coal cost, $/$10^6$ Btu	2.61	2.61

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[a] A variety of sorbents can be used with LIMB.
Costs for alternate sorbents are indicated on Figures 2 and 3 and in Table 6.

Table 5

BOILER AND COAL CHARACTERISTICS SELECTED FOR LIMB AND FGD ECONOMIC ANALYSIS

			Coal Characteristics		
Unit Size, MWe	Status	Net Plant Heat Rate, Btu/kW•h	High Heating Value Btu/lb	% S	% Ash
300	Retrofit	9,500	11,700	3.36	15.14
300	Retrofit	9,500	11,700	1.92	15.08
500	New	9,500	11,700	1.92	15.08
500	New	10,500	8,200	0.48	6.3

NOTE: Wall-fired boilers are used in these case studies.

Table 6

SORBENTS AND PERFORMANCE DATA USED FOR LIMB ECONOMIC ANALYSIS

Sorbent	Sorbent Cost, \$/ton	Retrofit Ca/S	Retrofit SO_2 Control, %	New Ca/S	New SO_2 Control, %
Vicron $CaCO_3$	18 [a]	2.5	45	-	-
Longview $Ca(OH)_2$	45	2.0	62	2.7	70
Longview $Ca(OH)_2$	45	-	-	4.0	82
Corson $Ca(OH)_2 \cdot Mg(OH)_2$	60	1.4	62	1.63	70 [b]
Corson $Ca(OH)_2 \cdot Mg(OH)_2$	60	-	-	2.1	82 [c]
Promoted $CaCO_3$	25	2.0	56	-	-
Promoted $Ca(OH)_2$	50	1.5	65	1.8	70 [b]
Promoted $Ca(OH)_2$	50	-	-	2.8	82 [c]

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a Actual cost used was \$17.88/ton.

b Minimum percent control required by NSPS for the 0.48% S coal.

c Minimum percent control required by NSPS for the 1.92% S coal to be at or below 260 ng/J (0.6 lb/10^6 Btu).

Table 7

COMPARISON OF COST COMPONENTS FOR RETROFIT LIMB AND FGD
Basis: 300 MWe Wall-fired Units at 62.8% Capacity Factor; 1985 Dollars

Technology	Sulfur, %	Sorbent	SO_2 Removal, $/ton	Total Capital Requirement, $/kW	15-Year Levelized Revenue Requirement, mills/kW•h[a]	15-Year Levelized Capital, mills/kW•h	15-Year Levelized Operating and Maintenance, mills/kW•h
FGD	1.92	$CaCO_3$	1359	210	17.30	6.10	11.20
LIMB	1.92	$CaCO_3$	1135	88	7.99	2.57	5.42
LIMB	1.92	$Ca(OH)_2$	844	79	8.14	2.30	5.84
LIMB	1.92	$Ca(OH)_2 \cdot Mg(OH)_2$	1101	89	10.61	2.59	8.02
LIMB	1.92	$CaCO_3$[b]	855	74	7.47	2.16	5.31
LIMB	1.92	$Ca(OH)_2$[b]	688	64	6.94	1.87	5.07
FGD	3.36	$CaCO_3$	829	239	20.22	6.97	13.25
LIMB	3.36	$CaCO_3$	874	107	10.81	3.11	7.70
LIMB	3.36	$Ca(OH)_2$	691	107	11.64	3.11	8.53
LIMB	3.36	$Ca(OH)_2 \cdot Mg(OH)_2$	942	122	15.87	3.55	12.32
LIMB	3.36	$CaCO_3$[b]	695	102	10.63	2.97	7.66
LIMB	3.36	$Ca(OH)_2$[b]	556	87	9.78	2.54	7.24

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[a] Includes levelized capital and levelized operating and maintenance charges.

[b] Promoted sorbent.

Table 8

COMPARISON OF COST COMPONENTS FOR NEW LIMB AND FGD
Basis: 500 MWe Wall-fired Units at 62.8% Capacity Factor; 1985 Dollars

Technology	Sulfur %	Sorbent	SO_2 Removal, $/ton	Total Capital Requirement, $/kW	30-Year Levelized Revenue Requirement, mills/kW•h[a]	30-Year Levelized Capital, mills/kW•h	30-Year Levelized Operating and Maintenance, mills/kW•h
FGD	0.48	$CaCO_3$	3715	158	15.97	4.39	11.58
LIMB	0.48	$Ca(OH)_2$	1134	19	4.87	0.54	4.33
LIMB	0.48	$Ca(OH)_2 \cdot Mg(OH)_2$	1366	21	5.87	0.58	5.29
LIMB	0.48	$Ca(OH)_2$[b]	961	18	4.13	0.49	3.64
FGD	1.92	$CaCO_3$	1377	170	17.53	4.73	12.80
LIMB	1.92	$Ca(OH)_2$	921	27	11.77	0.74	11.03
LIMB	1.92	$Ca(OH)_2 \cdot Mg(OH)_2$	1078	28	13.74	0.79	12.95
LIMB	1.92	$Ca(OH)_2$[b]	761	30	9.69	0.82	8.87

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[a] Includes levelized capital plus levelized operating maintenance charges.

[b] Promoted sorbent.

SESSION VII: SORBENT AVAILABILITY AND COSTS

Chairman, Richard Hooper, EPRI

AN UPDATE ON THE APPLICATION OF LIME PRODUCTS FOR SO_2 REMOVAL

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ABSTRACT

In the early years of utility SO_2 removal in the United States, scrubbing equipment manufacturers offered several "wet" processes utilizing different reagents. The most popular processes employed high calcium lime; magnesium modified lime; high calcium limestone; and sodium based alkalies as their scrubbing reagents. As in most industries where technology is continuously evolving, these processes have become more and more efficient, along with the commercialization of a major new process -- dry scrubbing. Because of the need for further SO_2 reductions from existing sources, new technologies are starting to be visualized and are receiving more laboratory and developmental attention. One of the more promising technologies involves the direct injection of lime-based absorbents into the hot flue gas stream.

The major objective of this discussion is to highlight current economics on today's most popular wet scrubbing systems with major emphasis on reagent aspects. Additionally, state-of-the-art technical and economic considerations on direct lime injection will be reviewed, with the commercial reagent emphasis centering on today's existing lime industry (location, tonnages, manufacturing processes, etc.). The question of lime manufacturing flexibility to meet current and projected lime demand will be discussed with respect to assumed commercialization of direct lime injection technology.

With these variables in better perspective, it can be seen that today's lime industry is attuned to SO_2 removal reagent needs, and will readily respond to the anticipated needs for lime-based alternative absorbents.

INTRODUCTION

In the early years of electric utility-based SO_2 removal in the United States, scrubbing equipment manufacturers offered several "wet" processes utilizing different reagents. The most popular processes employed high calcium lime; magnesium modified lime; high calcium limestone; and sodium based alkalies as their scrubbing reagents. As in most industries where technologies are continually evolving, these processes have become more and more efficient; along with the commercialization of a major new process -- spray drier scrubbing, i.e., dry scrubbing. Because of the need for further SO_2 reductions from existing sources and their unique retrofit requirements, new technologies are starting to be visualized and are receiving tremendous laboratory and developmental attention. One of the more promising technologies involves the direct injection of lime based absorbents into the hot flue gas stream, i.e., dry injection.

The major objective of this discussion is to highlight current state-of-the-art technical and economic considerations of dry lime injection with respect to the commercial lime industry. In order to understand the lime industry, a brief overview of the industry will be undertaken discussing the major manufacturing processes, locations, markets, new technology, etc. Additionally, projected demand for lime products with respect to various acid rain demand scenarios will be presented.

The assumption throughout this discussion is that, if one were to go commercial with dry lime injection technology today, lime-based products, calcium hydrate and dolomitic hydrate, are the only reagents that can meet the general process goals of 60 to 70 percent SO_2 removal at a 2 to 1 calcium to sulphur mole ratio based on inlet SO_2 concentrations.

IDENTITY OF THE LIME INDUSTRY

As is quite typical of many industries, what they do and what they manufacture may be confused with other industries. To help clarify the lime industry, lime manufacturing typically involves three major operations:
(1) Quarrying or mining the starting natural resource -- limestone.
(2) Manufacturing the limestone into a finished product -- quicklime.
(3) Remanufacturing of the quicklime into lime based products -- hydrates.
Two words have been mentioned that are often confused with one another -- limestone and quicklime. Limestone is the natural resource that is found in the earth. It is a carbonaceous rock of varying calcium carbonate content; typically greater than 90% calcium carbonate ($CaCO_3$). A common species intergrained with many limestones is magnesium carbonate ($MgCO_3$). Depending upon the magnesium carbonate concentration (usually greater than 40%), the limestone may be called "dolomitic limestone." Dolomitic and calcium limestones are mined, processed, and handled in similar ways. However, the calcining conditions vary, depending upon the desired product. For purposes of this discussion, emphasis will be placed on high calcium quicklime or lime products that usually contain less than 2.5% by weight magnesium oxide. However, current experimental data on dry injection indicates that dolomitic products are applicable. Process economics, based on delivered prices of each, may greatly influence the choice of reagent, high calcium or dolomitic lime products. The delivered price will be influenced by the transportation cost from the closest lime producer, dolomitic or high calcium.

The initial lime manufactured product, quicklime, calcium oxide (CaO), is not found in nature. The chemical conversion process from limestone to lime involves the heating of limestone to a minimum of 1,652°F (900°C) to liberate the carbon dioxide and to produce the highly active quicklime. Quicklime readily reacts with water or water vapor to form the lime product, calcium hydroxide [$Ca(OH)_2$].

In 1983, lime in its oxide or hydrate form was the number three (3) ranked industrial chemical. Table 1, Leading Lime Uses In 1983, (attached) tabulates the latest statistics on the uses of lime. The environmental uses of lime; sulphur removal, sewage treatment, water purification, and acid water treatment, amount to 22.5% of the total market, or 3,353,000 tons of lime. Of this 22.5%, approximately 30%, is devoted to SO_2 removal -- 1,019,000 tons. This is illustrated in Figure 1, U.S. Environmental Uses Of Lime, (attached).

Lime for SO_2 removal is already a significant part of the lime industry and emphasizes the lime industry's commitment to the FGD industry. Figure 2, Commercial Lime Plants In The U.S. & Canada, (attached) depicts the location of the commercial lime industry. These plants are quite widespread and FGD lime needs can be met from existing capacity. Currently, it is estimated that the commercial lime industry in the Continental United States can supply an additional five million tons per year of quicklime from their existing capacity. It is envisioned that additional dry lime injection needs will be met from capacity expansions at presently existing lime production facilities.

LIME PRODUCTION

As in any supplier-user situation, and more so in the case of long-term FGD contracts, it is important to understand each others production modes. Figure 3, Lime Manufacture Flow Sheet, (attached) outlines the various steps that are needed to manufacture high quality quicklime and lime products. This operation is not quite as simple as digging up limestone, heating it, and delivering the product to the customer. Although not emphasized on this flow sheet, there are numerous quality control check points, such as stone sizing, quicklime testing to meet production guidelines, and delivery testing to assure the product meets the customer specifications according to ASTM, AWWA, TAPPI, etc., procedures.

This flow sheet can also be classified into four major areas:

1. Precalcination limestone preparation
2. Calcination of the limestone
3. Product classification
4. Hydrate production

Precalcination limestone preparation can generally be termed quarrying or mining of the raw stone, plus stone sizing for the particular type of calcining device (kiln). Depending upon the limestone depth below the earth's surface, the lime producer will use quarrying or underground mining methods to extract limestone from its natural bed. Figures 4-7 (attached) depict various practices in producing the right quality of stone prior to calcination. The overall intent of this phase of lime production is to produce the right size of stone that can most efficiently be calcined into lime in a particular type of kiln while minimizing the waste limestone (fines).

At this point, the limestone has been prepared for calcination, or conversion, into quicklime. Briefly, calcination is the controlled liberation of carbon dioxide from the calcium carbonate portion of the limestone rock. Theoretically, this is accomplished by heating the stone to the dissociation temperature of approximately 1,652°F (900°C). There are several factors that affect this chemical conversion and dissociation temperature, but the rapid and continuous evolution of CO_2 gas is a major objective.

Based on the most recent survey of the National Lime Association, approximately 88% of the commercial producers use a calcining device called a rotary kiln to manufacture quicklime. This same poll indicated that the following types of fuels are used in lime calcination:

Table 2
Fuels Used for Kiln Firing

77.6%	Coal
15.2%	Natural Gas
5.6%	Bituminous or Petroleum Coke
1.6%	Oil

In conclusion, today the most prevalent type of calcining device in the United States and Canada is the rotary, coal-fired kiln.

Figure 8, Coal-Fired Rotary Preheater Kiln, (attached) is a cross section of a modern, preheater, rotary kiln. Sized limestone enters the preheater section above the feed end of the kiln. Hot kiln exhaust gases at 1,000-1,300°F preheat the stone before it enters the kiln and are reduced in temperature to approximately 350°F or less as they exit the preheater. It has been reported that as much as 20 to 50% of the calcining takes place in these preheater sections. As the stone rotates down the kiln, it may pass over a trefoil, dams, and/or lifters that have been designed into the internal refractory shell of the kiln to effect more transfer of the heat into the lime bed. As the calcined lime exits the kiln, it drops into a contact cooler where ambient air is forced, counter-currently, up through the hot lime bed. This cools the lime and the warm air is used for combustion air and coal drying. It is common for a properly designed and operated coal-fired, preheater kiln to consume about 4.5 to 5.5 million BTU/ton of lime.

SIZING, STORAGE, AND DELIVERY

At this point in the manufacturing process, the quicklime has been made and is cool; is now ready to be sized, portions converted to hydrate, stored, and delivered to customers. The choice of processing equipment and product sizes is usually dictated by the market and primary mode of delivery. Typical delivery modes are by covered hopper rail car, covered dump trucks, pneumatic trailer trucks, and to some extent, covered barges. Typical physical sizes available include 1 3/4" x 0, 3/4" x 0, 3/4" x 1/8" and 1/8" x 0. Screened quicklime products are also made into hydrated lime by adding a controlled amount of water. Both quicklime and hydrate are stored in large metal or concrete silos that are watertight and delivered in watertight equipment.

Transportation is always a consideration in bulk lime deliveries due to cost and the type of equipment utilized. Table 3, Typical Transportation Modes, lists the three major delivery modes, unit tonnages, delivery radius, and associated costs that are seen today by the lime industry.

Table 3
TYPICAL TRANSPORTATION MODES

	Tons/Shipment	Competitive Range (Miles)	Typical Costs ($/Ton Mile)
Truck	20- 25	0- 300	.06-.12
Rail	90- 100	100- 500	.04-.08
Barge	1,000-1,500	100-1,000	.01-.04

HYDRATE PRODUCTION

As hydrated quicklime is the final reagent material that is envisioned for dry injection, it is appropriate to look at today's commercial equipment used to make hydrate. Figure 9, Typical Flow Sheet Of A Lime Hydrating Plant, (attached), illustrates the flow and general equipment needed to produce normal calcium hydrate and normal dolomitic hydrate. Briefly, the starting quicklime product is gravimetrically metered into a premix chamber where the lime is rapidly mixed with an amount of water slightly in excess of the stoichiometrically required amount of water in order to complete the hydration process with little (less than 3 to 4%) moisture remaining in the product. As quicklime hydration is a violent, exothermic reaction, the premixed solids slurry proceeds into the seasoning chamber to complete the reaction and to fully utilize the reaction's exothermic heat to produce a dry, fluffy hydrate. At this point, the product can be stored and sold as is, or further processed, as shown, for controlled particle size distribution. Figure 10, Typical Equipment Arrangement of a Lime Hydrating Plant, (attached) depicts a compact layout for a hydration plant.

Dolomitic quicklime, $CaO \cdot MgO$, is a different compound and has different chemical properties. In particular, the heat of hydration is lower and atmospheric hydration equipment depicted above for high calcium quicklime is only sufficient to hydrate the calcium portion of the dolomitic molecule. This is commonly referred to as normally hydrated dolomitic lime. For complete hydration of both calcium and magnesium, steam pressures up to 100 PSI are typically used.

Figure 11, Flow Diagram of Pressure Hydration Process, illustrates a typical process. The major differences are the containment of the water/quicklime slurry, under pressure, and the release of the same for flash drying and particle size reduction. Referring to the flow sheet, dolomitic quicklime, usually of a finer size than used in normally hydrated products, is gravimetrically fed into a mixer for combination with water to form a thick paste. The paste is fed to a specially designed pump and pumped, under pressure, into the hydrating vessel. Unlike normal hydration, the mixture is retained in the hydrator for up to 30 minutes, as steam pressure builds and the hydration process continues. The hydrate is released into a collector/separator where the fine hydrate particles are separated from the steam and collected. Depending upon the use of the product, the hydrate may be sized and stored as is. or further reduced in size, classified, and stored for sale. Attached Tables 4 and 5 contain useful data on the properties of quicklimes and their resultant hydrates.

A recent survey by the National Lime Association of selected member companies indicated that pressure hydrated dolomitic products have surface areas ranging from 20 to 30 square meters per gram of product. The higher areas may be attributed to soft-burned, more reactive limes. Normal hydrated materials, high calcium and dolomitic, were found to possess slightly lower surface areas ranging from 15 to 20 square meters per gram. With respect to dry lime injection for SO_2 removal, indications are that particle surface area is an important process parameter but to what degree is yet to be determined. From a lime operators standpoint, normally hydrated materials are easier to manufacture.

Because of the varying bulk densities, flow properties, and tonnages involved in the lime industry's products, material handling is an important part of any system design. Each product -- stone, quicklime, and hydrate -- has its own distinct handling properties and each has to be considered separately in designing material handling systems. Extra consideration in designing a system will greatly reduce problems when the system starts into operation.

COMMERCIAL IMPLICATIONS OF DRY LIME INJECTION

In order to address the lime industry's ability to respond to dry lime injection's reagent demand, one must venture into unclear areas and make some decisions and/or assumptions about the potential impact of the acid rain issue on the lime industry. First, let us assume that an eight million ton per year reduction in 1980 emission levels will occur as outlined in Senate Bill 768 and will occur in the thirty-one state Acid Deposition Impact Region of the Eastern United States. Table 6, Example of SO_2 Reductions Resulting from Acid Rain Legislation, (attached) lists the expected tonnage impact of such legislation. The total SO_2 reduction amounts to roughly 10.2 million tons. Assuming that this total amount will be removed with dry lime injection, based on a calcium to sulphur stoichiometry of 2 for 60% SO_2 removal, the lime reagent tonnage is estimated at approximately 31.4 million tons of quicklime (based on 95% calcium oxide quicklime).

A more realistic scenario is probably closer to the one proposed by the Environmental Protection Agency assigning the SO_2 reductions to five various control technologies:
(1) LIMB
(2) Low NO_x Burners
(3) Physical Coal Cleaning
(4) Lime Spray Drying
(5) Wet Lime/Limestone FGD

Combining the eight million ton reduction requirement with the EPA's various technologies, Table VII assigns the removal requirements by control process.

Table 7
EPA Assumed Reductions By Control Process

Control Process	Reduction (MM Tons)
LIMB	3.0
Low NO_x Burners	0.5
Physical Coal Cleaning	1.0
Lime Spray Drying	3.0
Wet Lime/Limestone FGD	0.5
Total SO_2 Reductions/Year	8.0

The assignment of these amounts is based on using the least costly (assumed to be LIMB) to the most expensive (wet FGD) to a limit of about 50% of the estimated maximum capability as estimated by the EPA. If additional removals beyond this eight million tons are required, these will be assigned to wet lime/limestone FGD.

For purposes of this discussion, we can then combine the Senate Bill 768 tonnages with the EPA's estimates as listed in Table 8.

Table 8
Estimated Overall Reductions By Control Process

Control Process	Reduction (MM Tons)
LIMB	3.0
Low NO_x Burners	0.5
Physical Coal Cleaning	1.0
Lime Spray Drying	3.0
Wet Lime/Limestone FGD	2.7
Total SO_2 Reductions/Year	10.2

Analyzing the Bureau of Mines Minerals Yearbook section on lime for the past several years, and discussions with The National Lime Association, it is estimated that the commercial lime industry currently has approximately five million tons per year excess capacity. Further, breaking this excess capacity down into regions closely matching those areas in the Acid Deposition Impact Region, it is estimated that four million tons of excess capacity exist in the region east of the Mississippi. Figure 12, 1984 Uncommitted Lime Capacity, illustrates this geographic distribution.

Based on this estimate, the lime industry has immediate capacity to handle the initial phases of SO_2 reduction due to this assumed acid rain legislation. As lime spray drying technology is commercially accepted now, this lime capacity could now meet 74% of Table VIII's projected spray drying demand without adding additional capacity.

Since there are numerous lime plants in the eastern half of The United States, especially in the Midwest and Mid-Atlantic states, it is felt that additional lime needs will be filled by expanding calcining and/or hydrating capacity at existing production facilities as they now exist. This will minimize capital cost and result in lower lime reagent costs for SO_2 removal. These costs can be further minimized if these new kilns can be completely dedicated to a particular user or a consortium of users within a particular geographic area.

Based on the assumptions presented in this discussion for dry lime injection and lime spray drying (Table 8) with 100% acceptance of these technologies as known today, 1995 lime demand is estimated at 14.6 million tons per year. Utilizing today's estimated excess capacity and continuing to meet other markets, this represents a lime short fall of approximately 10.6 million tons per year in 1995.

The cost of such an expansion is difficult to estimate due to the size of a kiln needed at a particular location to meet demands within a specific geographic area. For example, a 500 megawatt station required to obtain 60% removal of inlet SO_2 burning 2.5% sulphur coal and employing dry lime injection technology with a two to one stoichiometry may consume 109,000 tons/year of lime(CaO) on a 95% calcium oxide basis. This would represent a 330 ton per day kiln demand. A single kiln of this size could easily be constructed, but it may be more economical to construct a larger kiln in the range of 600 to 1,000 tons per day capacity. Thus, the estimated 1995 demand for 10.6 million tons of lime might be met by installing 50 to 60 additional kilns of the 600 ton/day capacity type. This represents a 20 to 25% increase in the number of kilns in the United States and can be easily handled by today's lime industry over the next ten years.

CONCLUSION

In this brief discussion, an effort has been made to reaffirm that the lime industry has been involved with the utility industry for many years, by supplying high quality lime products for SO_2 removal with conventional wet lime scrubbers and the newer spray dryers. From the description of the lime manufacturing process, it is evident that today's lime industry is attuned to the ever present need for efficient manufacturing processes and employs some of the most modern and efficient systems in the world.

To meet the impending needs for additional lime requirements, the lime industry is well positioned in the eastern half of the United States with immediate production capacity to handle new dry lime injection or spray drier applications. For the more distant applications in the 1990's, the most economical approach to lime supply is to expand at the present quarrying and production facilities by adding kiln capacity. Based on the projections just discussed, this 20 to 25% expansion can be quite manageable with prudent planning.

In conclusion, the lime industry is a dynamic industry that has conquered the energy crisis of the '70's. It has the awareness and existing production capacity to meet the immediate needs of this new dry lime injection process. And most importantly, it is willing to commit its resources to assure industry that lime will be available when it is needed at competitive prices to meet the future requirements.

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6. Internal Communications, National Lime Association, Arlington, Virginia.

7. Internal Communications, Southern Research Institute, Birmingham, Alabama.

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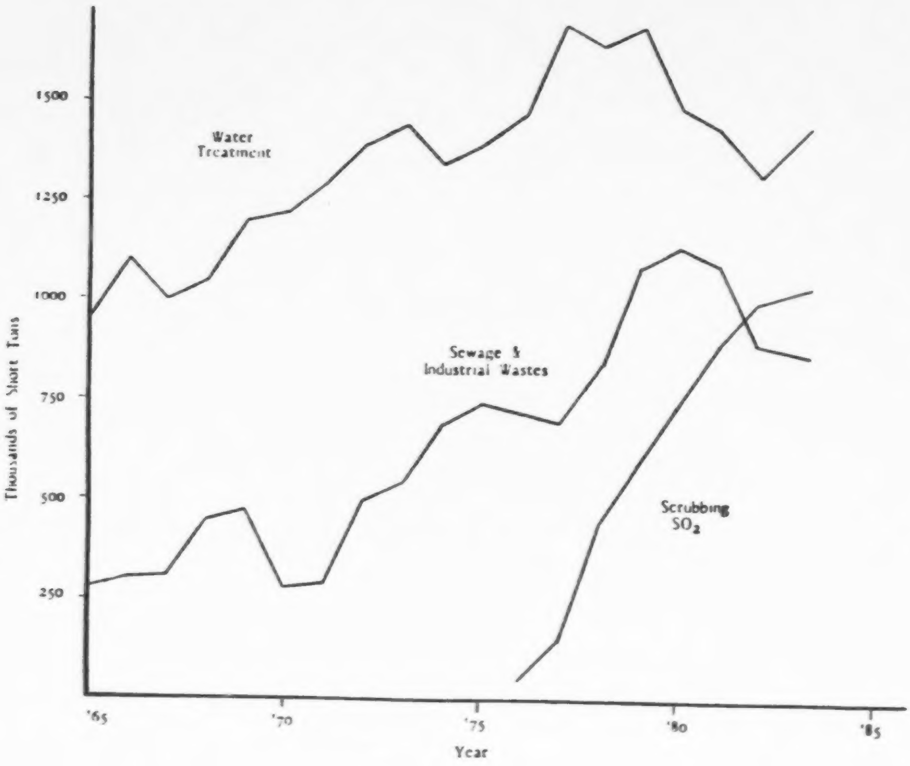

Figure 1. U.S. Environmental Uses of Lime

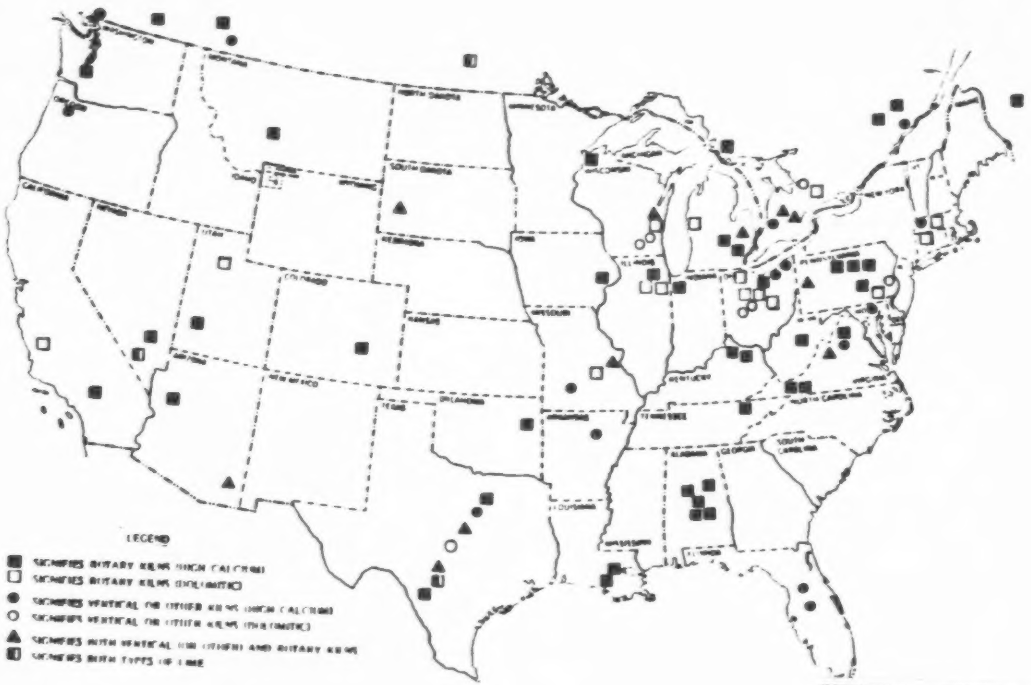
LEGEND
■ SIGNIFIES ROTARY KILNS (HIGH CALCIUM)
□ SIGNIFIES ROTARY KILNS (DOLOMITIC)
● SIGNIFIES VERTICAL OR OTHER KILNS (HIGH CALCIUM)
○ SIGNIFIES VERTICAL OR OTHER KILNS (DOLOMITIC)
▲ SIGNIFIES BOTH VERTICAL (OR OTHER) AND ROTARY KILNS
◧ SIGNIFIES BOTH TYPES OF LIME

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Figure 2. Commercial Lime Plants in U.S. and Canada

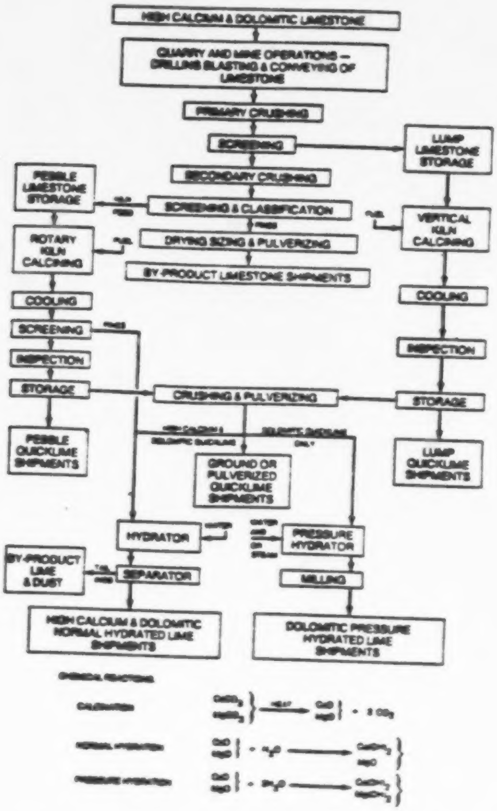
HIGH CALCIUM & DOLOMITIC LIMESTONE
QUARRY AND MINE OPERATIONS — DRILLING BLASTING & CONVEYING OF LIMESTONE
PRIMARY CRUSHING
SCREENING
LUMP LIMESTONE STORAGE
SECONDARY CRUSHING
PEBBLE LIMESTONE STORAGE
SCREENING & CLASSIFICATION
VERTICAL KILN CALCINING
ROTARY KILN CALCINING
DRYING SIZING & PULVERIZING
BY-PRODUCT LIMESTONE SHIPMENTS
COOLING
SCREENING
INSPECTION
STORAGE
CRUSHING & PULVERIZING
PEBBLE QUICKLIME SHIPMENTS
GROUND OR PULVERIZED QUICKLIME SHIPMENTS
LUMP QUICKLIME SHIPMENTS
ONLY
HYDRATOR
PRESSURE HYDRATOR
BY-PRODUCT LIME & DUST
SEPARATOR
MILLING
HIGH CALCIUM & DOLOMITIC NORMAL HYDRATED LIME SHIPMENTS
DOLOMITIC PRESSURE HYDRATED LIME SHIPMENTS

Figure 3. Lime Manufacture Flow Sheet

Figure 4. Quarry Mining

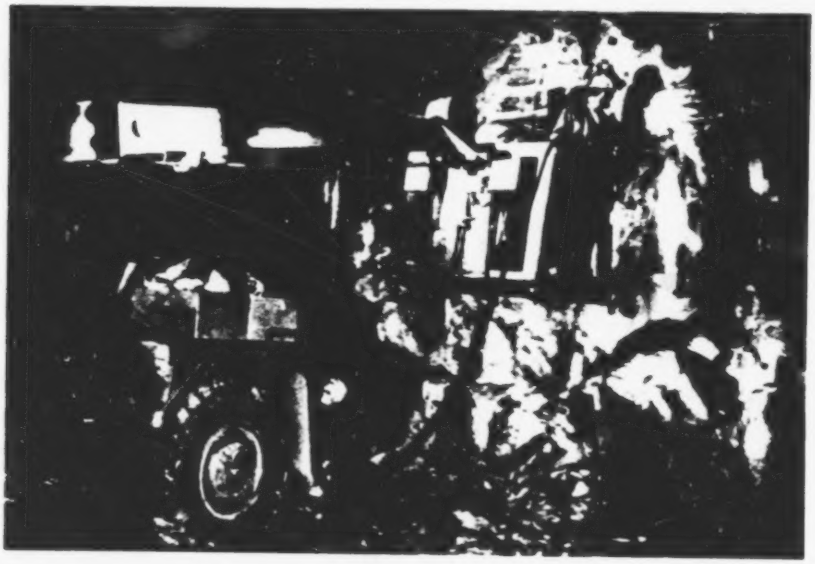

Figure 5. Underground Mining

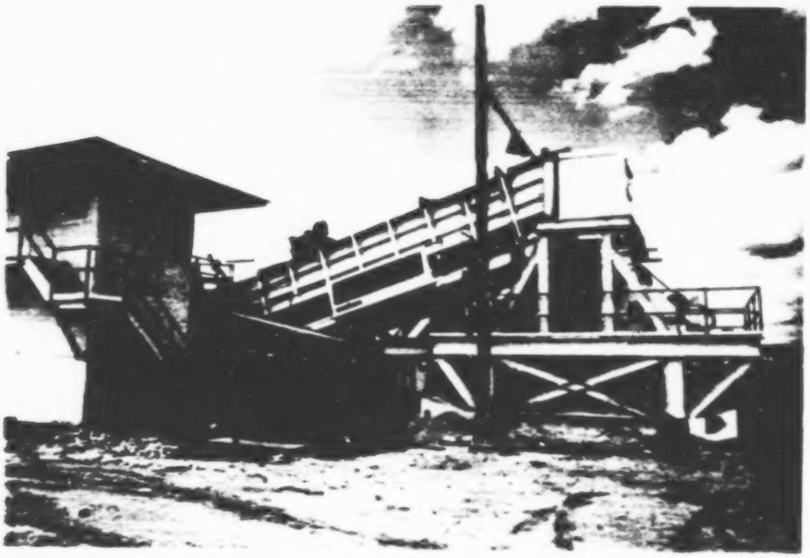

Figure 6. Primary Roll Crusher

Figure 7. Kiln Feed Preparation

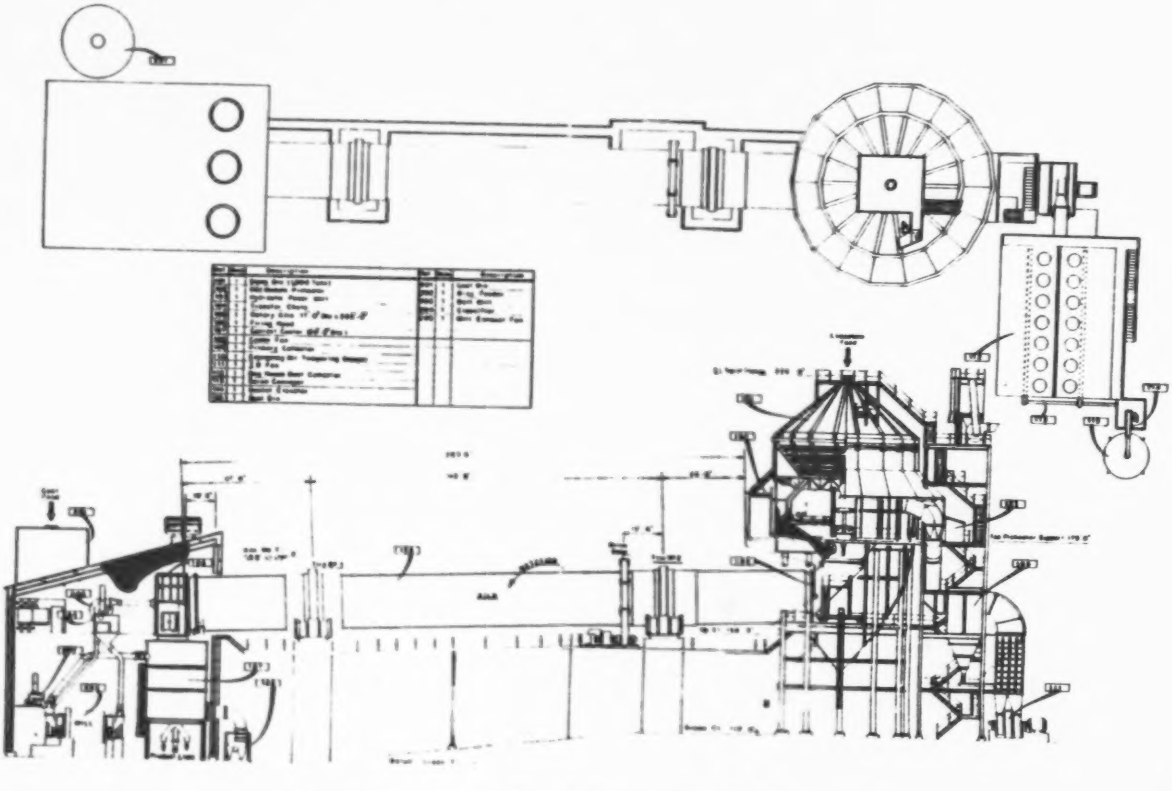

Figure 8. Coal-fired Rotary Preheater Kiln

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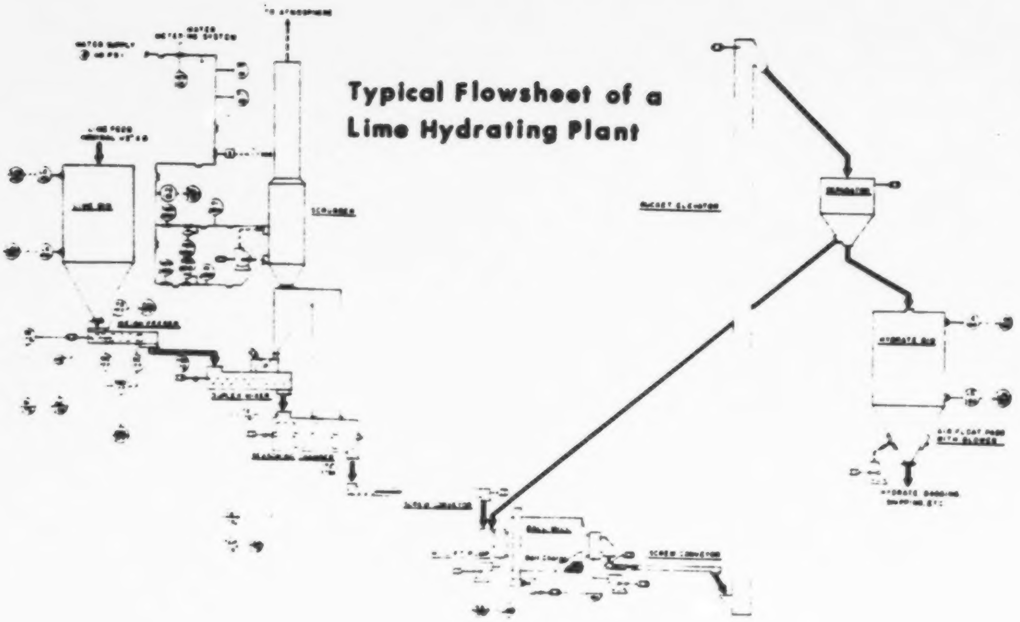
Typical Flowsheet of a Lime Hydrating Plant
TO ATMOSPHERE
SCRUBBER
BUCKET ELEVATOR
SEPARATOR
HYDRATE BIN
BALL MILL
SCREW CONVEYOR

Figure 9. Typical Flowsheet of a Lime Hydrating Plant

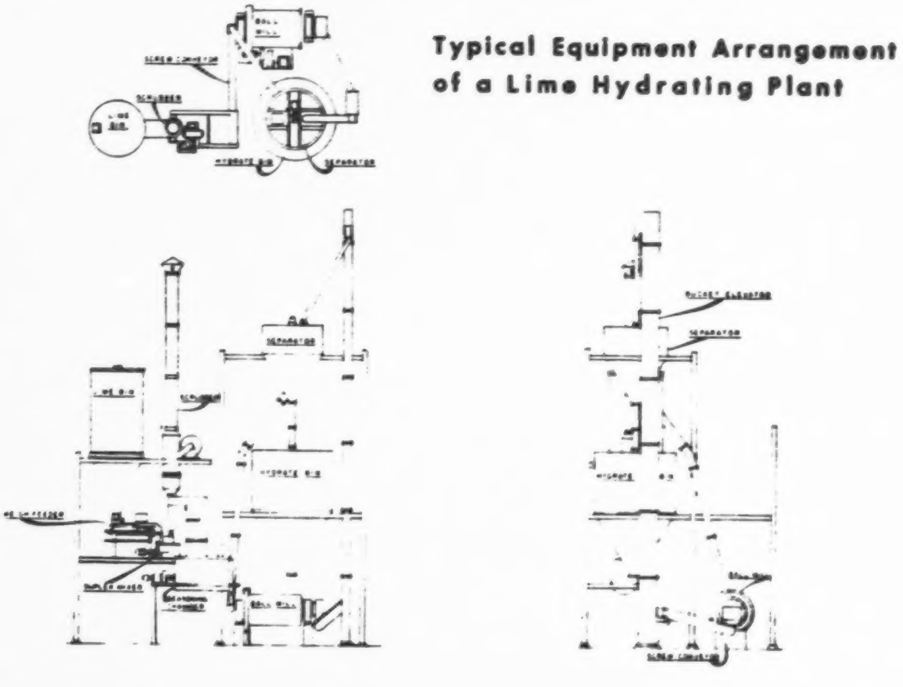
Typical Equipment Arrangement of a Lime Hydrating Plant
BALL MILL
SCREW CONVEYOR
SCRUBBER
LIME BIN
HYDRATE BIN
SEPARATOR
BUCKET ELEVATOR

Figure 10. Typical Equipment Arrangement of a Lime Hydrating Plant

FLOW DIAGRAM
OF
PRESSURE HYDRATION PROCESS

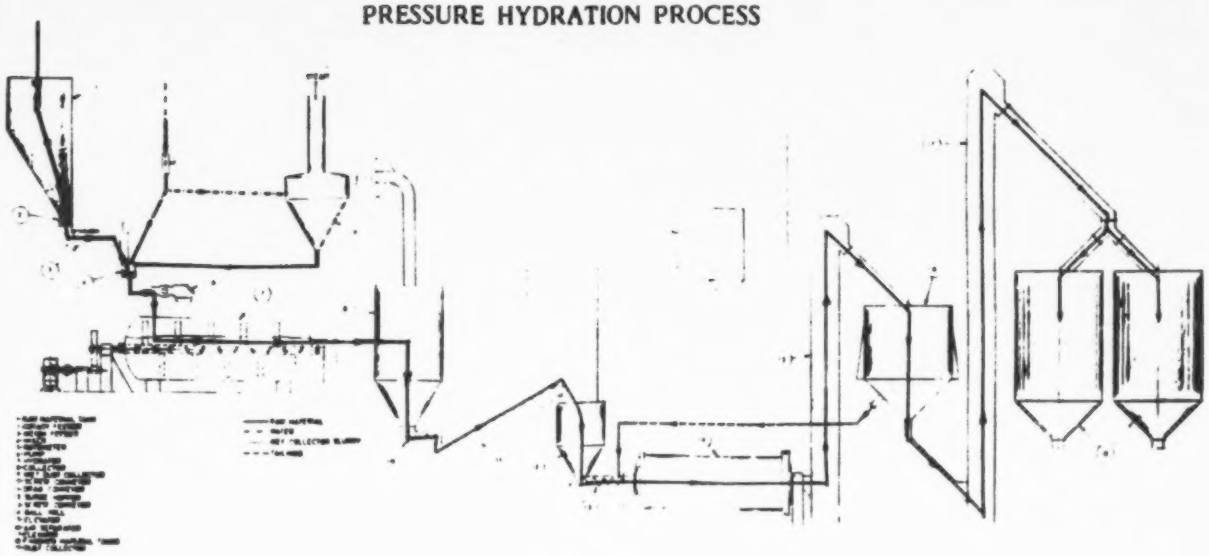

Figure 11. Flow Diagram of Pressure Hydration Process

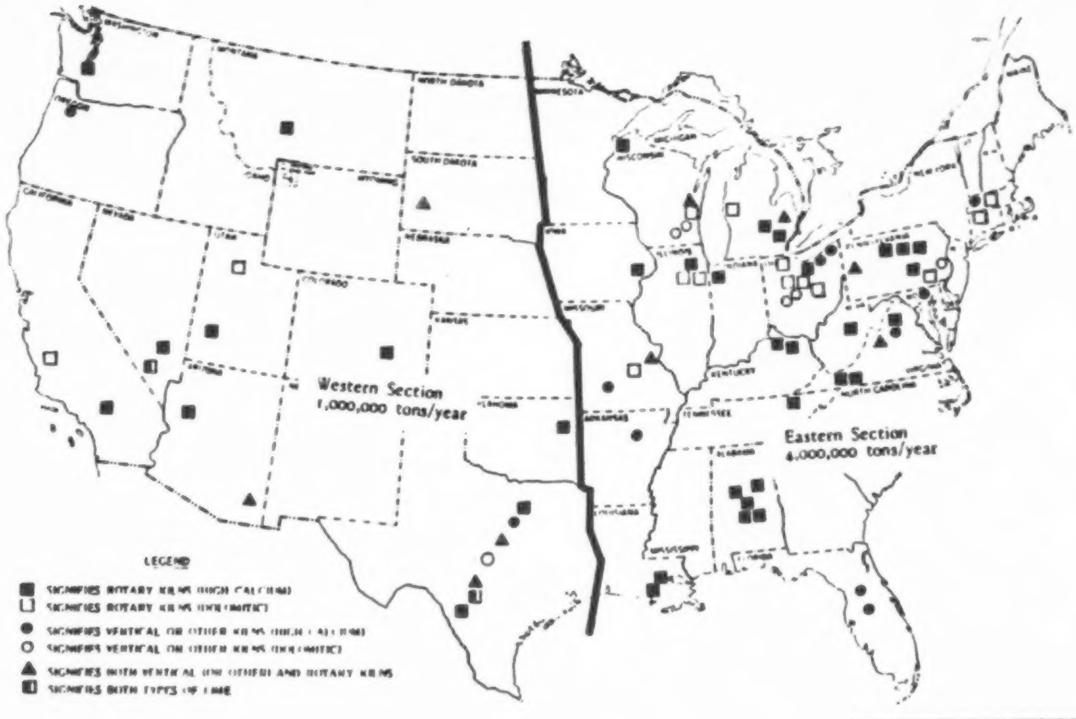
Western Section
1,000,000 tons/year
Eastern Section
4,000,000 tons/year
LEGEND
■ SIGNIFIES ROTARY KILNS (HIGH CALCIUM)
□ SIGNIFIES ROTARY KILNS (DOLOMITIC)
● SIGNIFIES VERTICAL OR OTHER KILNS (HIGH CALCIUM)
○ SIGNIFIES VERTICAL OR OTHER KILNS (DOLOMITIC)
▲ SIGNIFIES BOTH VERTICAL (OR OTHER) AND ROTARY KILNS
◧ SIGNIFIES BOTH TYPES OF LIME

Figure 12. Uncommitted Lime Capacity

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Table 1

LEADING LIME USES IN 1983*

	Use	Tons (1000's)	% of Total
1.	Steel	5,393	36.2
2.	Water Purification**	1,488	10.0
3.	Sulfur Removal **	1,019	6.8
4.	Pulp and Paper	916	6.1
5.	Soil Stabilization	807	5.4
6.	Sewage Treatment**	578	3.9
7.	Sugar Refining	566	3.8
8.	Alkalies	560	3.8
9.	Magnesium from Seawater	557	3.7
10.	Refractory Dolomite	418	2.8
11.	Copper Ore Concentration	390	2.6
12.	Building Lime	378	2.5
13.	Acid Water Treatment**	268	1.8
14.	Calcium Carbide	209	1.4
15.	Aluminum and Bauxite	203	1.4
16.	Magnesium Metal	171	1.1
17.	Glass	156	1.0
18.	Precipitated Calcium Carbonate	128	0.9
19.	Ore Concentration	80	0.5
20.	Oil and Grease	52	0.3
21.	All Other Uses	565	4.0
	Total	14,902	100.0

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* Source - 1983 Bureau of Mines Minerals Yearbook - Lime Section

** Environmental Uses - 3,353,000 tons = 22.5% of Total

Table 4

PROPERTIES OF THEORETICALLY PURE LIME COMPONENTS

	PURE LIME			
PROPERTIES	QUICKLIME COMPONENTS		HYDRATED LIME COMPONENTS	
Chemical Name	Calcium Oxide	Magnesium Oxide	Calcium Hydroxide	Magnesium Hydroxide
Chemical Formula	CaO	MgO	$Ca(OH)_2$	$Mg(OH)_2$
Molecular Weight	56.08	40.32	74.096	58.336
Melting Point	2570°C (4658°F)	2800°C (5072°F)		
Decomposition Point			580°C (1076°F)	345°C (653°F)*
Boiling Point	2850°C (5162°F)	3600°C (6512°F)		
Refractive Index	1.838	1.736	1.574 and 1.545	1.559 and 1.580
Heat of Solution at 18°C.	+ 18.33 kg.-cal.		+ 2.79 kg.-cal.	-0.0 kg.-cal.
Crystalline Form	cubic	cubic	hexagonal	hexagonal
Density	3.40	3.65	2.343	2.4

*There is not complete agreement on the exact decomposition point of $Mg(OH)_2$, however, the value given represents the best data available.

Table 5

PROPERTIES OF TYPICAL COMMERCIAL LIME PRODUCTS

QUICKLIMES

	High Calcium	Dolomitic
Primary Constituents	CaO	CaO and MgO
Specific Gravity	3.2-3.4	3.2-3.4
Bulk Density (Pebble Lime) lb./cu. ft.	55-60	55-60
Specific Heat at 100°F Btu/lb.	0.19	0.21
Angle of Repose	55**	55**

HYDRATES

	High Calcium	Normal Dolomitic	Pressure Dolomitic
Primary Constituents	$Ca(OH)_2$	$Ca(OH)_2 + MgO$	$Ca(OH)_2 + Mg(OH)_2$
Specific Gravity	2.3-2.4	2.7-2.9	2.4-2.6
Bulk Density lb/cu. ft.	25-35**	25-35**	30-40**
Specific Heat at 100°F Btu/lb.	0.29	0.29	0.29
Angle of Repose	70**	70**	70**

*The angle of repose for both types of lime (hydrate in particular) varies considerable with mesh, moisture content, degree of aeration and physical characteristics of the lime. (E.G., for quicklime it generally varies from 50° to 55° and for hydrated lime it may range as much as 15° to 80°.)

**In some instances these values may be extended. The Scott method is used for determining the bulk density values. In calculating bin volumes the lower figure should be used.

Table 6

EXAMPLE OF SO_2 REDUCTIONS RESULTING FROM ACID RAIN LEGISLATION

	1980 SO_2 Emissions	8 MM ton SO_2 Reduction (tons SO_2 x 1000)	Emissions Growth 1980-95 (tons SO_2 x 1000)	Total Reduction Required (tons SO_2 x 1000)	Percent of 1980 Emissions Reduction Required
Alabama	739.8	210.3	-81.2	129.1	17
Arkansas	78.9	2.0	97.5	99.5	126
Connecticut	149.1	0.0	19.7	0.0	0
Delaware	90.8	11.9	15.3	27.2	30
District of Columbia	44.4	0.0	0.0	0.0	0
Florida	933.7	267.4	271.7	539.1	58
Georgia	837.7	350.1	150.0	500.1	60
Illinois	1,532.8	611.8	-37.6	574.2	37
Indiana	2,079.8	1,145.2	-37.3	1,107.9	53
Iowa	344.3	93.9	23.4	117.3	34
Kentucky	1,108.0	544.9	-40.5	504.4	46
Louisiana	260.5	0.1	252.2	252.3	97
Maine	98.4	1.4	-25.6	-24.3	0
Maryland	330.0	76.8	66.2	143.0	43
Massachusetts	477.7	63.2	71.1	134.3	28
Michigan	931.7	177.6	154.2	331.8	36
Minnesota	294.0	36.4	20.0	56.4	19
Mississippi	196.1	70.3	178.4	248.7	127
Missouri	1,348.6	779.6	132.5	912.1	68
New Hampshire	109.0	34.3	4.2	38.5	35
New Jersey	362.0	28.1	76.5	104.6	29
New York	1,078.9	125.9	66.0	191.9	18
North Carolina	618.5	19.0	83.9	102.9	17
Ohio	2,802.6	1,366.0	405.4	1,771.4	63
Pennsylvania	2,165.6	618.5	-107.6	510.9	24
Rhode Island	32.1	0.0	3.7	0.0	0
South Carolina[1]	315.6	63.2	48.6	111.8	35
Tennessee	1,086.0	526.3	25.0	551.3	51
Vermont	15.0	0.0	0.5	0.0	0
Virginia	326.7	5.5	102.1	107.6	33
West Virginia	1,093.6	456.8	99.1	555.9	51
Wisconsin	618.8	286.8	212.3	499.1	81
Total	22,500.7	7,949.5	2,249.2	10,199.0	45[1]

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[1] average

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DRY INJECTION FGD SODIUM-BASED SORBENTS:
AVAILABILITY AND ECONOMIC EVALUATION

R.M. Wright
FMC Corporation
Alkali Chemicals Division
Philadelphia, Pennsylvania

INTRODUCTION

Injection of a dry pulverized sodium sorbent into the flue gas ahead of a fabric filter to collect SO_2 in conjunction with the fly ash is receiving more and more attention from both the utility industry and potential suppliers of systems and sorbents. As evidence of both the commercial viability and the substantial cost savings mounts, it naturally heightens the interest in all involved.

Dry injection SO_2 scrubbing, as it is now known, is not especially new in concept. The idea of using a dry sorbent to remove the SO_2 goes back many years.

When fabric filters grew in interest, attention turned from fluid bed and regenerable fixed bed reactors to direct injection of the dry sorbent into the gas stream with subsequent collection along with the fly ash. A number of lab and pilot studies were conducted to prove out the basic concept. The work culminated in a 22 MW demonstration at the Cameo Unit 1 of Public Service of Colorado. This test program, under the sponsorship of EPRI showed that dry injection is technically practical. A subsequent economic study by Stearns-Roger added the icing. Not only is it workable, dry injection is less costly by 20% over lime spray dryer scrubbing.

The only problem was that at the time the Cameo work was done there was no one offering a sorbent that was available. That was three years ago and a lot has changed. Today there are several suppliers offering commercial quantities of products to use as dry injection sorbents and I believe we have only touched the surface.

This paper will describe the potential sorbents, their sources and availability, and finally the factors that go into evaluating the sorbent cost to the utility or other user.

SORBENTS

The heart of dry injection is the sorbent. Chemically the molecule that is removing the SO_2 is sodium carbonate. The reaction that takes place is:

$$Na_2CO_3 + SO_2 \dashrightarrow Na_2SO_3 + CO_2$$

But the Cameo tests showed very little reaction between commercially available sodium carbonate (soda ash) and SO_2.

Fortunately there are a number of other sodium chemicals that will convert to sodium carbonate under relatively mild heating conditions such as found in the hot flue gas. These chemicals are any combination of sodium carbonate and sodium bicarbonate ($NaHCO_3$). And indeed there may be ways found to make soda ash itself work.

The sorbent choices are numerous. Table I lists the known chemical combination of sodium carbonate and sodium bicarbonate that are relatively stable. All will decompose with heat to form sodium carbonate. The time and temperature needed to achieve the full calcination varies with compound but all can be fully converted with the residence time and temperature in a typical baghouse.

In addition to these pure chemical compounds several of these occur naturally as ores. Just to confuse things the ores have different names. Table II lists these. To describe the source and availability of the various sorbents we will begin with the ore from which the sorbents originate.

Trona - Wyoming

Trona is the only ore that is being commercially mined today. Commercial deposits have been located in south western Wyoming and in Southern California. The Wyoming deposit is the remains of a huge ancient lake. The deposit was discovered in the late 30's and the first commercial plant was completed in 1953 by FMC. Today five companies mine greater than 12 million tons of trona per year.

The trona is deposited in numerous relatively thick flat beds. The commercially mined beds are located 800-1500 ft. below ground and are dry mined using many techniques. This vast reserve contains an estimated 52 billion tons of trona.

The trona ore as mined is relatively pure containing roughly 85 percent sodium sesquicarbonate. There are a few tenths percent of soluble salts, primarily sodium sulfate and sodium chloride. The majority of the impurities are insoluble with dolomite and calcite making up 85 percent of the insolubles.

The impurities have some important effects that need to be considered. The costs of transportation and waste disposal are greater because of the extra volume of material. Also the impurities are not as easily pulverized as the crystalline sodium salt. This may require sizing with a larger grinder and higher power consumption. The extra grain loading on the fabric filter was shown at Cameo to not require a larger baghouse for satisfactory performance.

Several techniques are available to beneficiate trona to a higher purity. None are practiced today but could be used if the improvement in value (lower transportation, disposal and power costs) warrants.

None of this trona is shipped presently. Rather it all goes into making soda ash or sodium sesquicarbonate. Companies would need to add handling and loading equipment to make it available for large scale rail shipment to a utility. It might also be appropriate to do some size reduction at the mine site. Complete pulverization is not expected to be suitable because of the handling problem. In addition, if the bulk density gets too low the transportation cost rises.

The surface processes to convert trona into products are important to review. There are two basic processes that are used by the five producers. They are termed the monohydrate process and the sesqui process. The monohydrate process is employed by all producers whereas only FMC uses the sesqui process in addition to the monohydrate process.

The monohydrate process (Figure I) calcines the trona to crude soda ash before dissolving and removing the insoluble impurities. The sodium is recovered by crystallization of sodium carbonate monohydrate (hence the process name). Finally the monohydrate is heated to remove the water and yield soda ash.

Two solid intermediates are prepared in the course of this process: crude soda ash and sodium carbonate monohydrate. If either were suitable sorbents they could be made available relatively easily and in large volumes.

The sesqui process (Figure II) differs in that no chemical change (calcination) occurs until after the impurities and the recrystallization takes place. The pure sodium sesquicarbonate crystals are then heated to convert them to soda ash. Only one solid intermediate is produced in this process: sodium sesquicarbonate. This intermediate is identical to trona except that the impurities have been removed. It was successfully tested at Cameo and is available in very large quantities as with other soda ash intermediates.

An additional sodium chemical is produced by two Wyoming producers. It is sodium carbonate decahydrate. FMC dredges about 500 M tons per year off the floor of their evaporation lake. Allied crystallizes deca from their purge stream. Presently both return the deca to their process to improve efficiency but the deca could also be supplied if found suitable as a dry injection sorbent.

Trona - Southern California: Owens Lake

Two dry lake beds in Southern California contain large deposits of trona that are commercially recoverable. Owens Lake is presently being mined by Cominco American. The deposit is on the surface of the lake and contains reserves of 50-60 million tons. A section is allowed to drain to remove entrained brines. The trona is removed and air dried to make it handleable.

The composition of the trona is different than that in Wyoming. Purity is 60-70 weight percent sodium sesquicarbonate. Impurities consist of Na_2SO_4, 5-7%; NaCl, 4-6%; free water,2-10%; and insolubles, 6-10%. The trona is shipped to customers without further processing.

Cominco has stated they could add additional drying and beneficiating (up to about 85% purity) if needed. To provide different products from this plant would require a major capital investment to build the necessary processing plant.

Trona - So. Calif. - Searles Lake

Searles Lake is another dry alkaline lake bed that was formed at the same time as Owens Lake. The existing operation at Searles Lake is quite different from Cominco's. Kerr-McGee has two plants, Argus and West End, that are recovering sodium carbonate values from the lake.

Argus is solution mining a trona bed about 350 feet below the lake surface. West End is mining at shallower depths in a mixed salt layer. Both brines are carbonated to crystallize out the sodium carbonate values as sodium bicarbonate. The primary differences in the bicarb from the two plants is in the level of impurities in the crystals, West End being higher.

The bicarb at Argus is presently only used as an intermediate in the production of soda ash. The bicarb is converted to light soda ash followed by sodium carbonate monohydrate and then, as with Wyoming producers, calcined to soda ash. West End does not go through the monohydrate step.

Any of these intermediates, bicarb, light soda ash, or monohydrate could be relatively easily prepared for use as a sorbent in dry injection scrubbing. Bicarb, of course, was successfully tested at Cameo (as nahcolite).

The two Kerr McGee plants have a combined capacity for soda ash of 1.4 million tons backed by an estimated reserve at Searles Lake of 900 million tons.

Nahcolite

In the northwestern part of Colorado is located an area containing a very large deposit of bedded and dispersed nahcolite. This area has been of commercial interest for many decades both for the nahcolite and more importantly for the rich oil shales present.

Despite this long interest, no commercial mining has yet taken place. This is mostly due to the costs of dry mining nahcolite at its greater depths and lower assay and converting it into soda ash compared to Wyoming trona.

Industrial Resources, Inc. is developing a solution mining process that may improve the economics if technically successful. They report the successful completion of the first phase pilot and are going to begin the second phase soon.

Whereas the dry mined nahcolite was of an assay of about 70%. A product from IRI's solution mining project would more appropriately be termed sodium bicarbonate because the purity would be expected to be quite high.

Natrona, Inc. is also interested in solution mining of their nahcolite lease. They have not yet begun field testing of the process they plan to use. They have licensed the Shell mining technology that was worked on several years ago in conjunction with an oil shale project.

Of more potential impact on costs than solution mining would be a major shale oil project in the nahcolite zone. Such a project might yield nahcolite bearing ores on the suface at zero (or low) assigned cost. The low price for crude, the immense capital for such projects and the Federal ownership of essentially all the nahcolite zone make a venture improbable in the next ten years.

Despite the great potential of nahcolite, until further evaluation shows its economic viability, it cannot be counted on to be available as a sorbent.

Other Ores

Wegscheiderite, natrol and thermonatrite are all minerals that have been found in nature. None have been found in sufficient concentrations or large enough deposits to be economically recoverable.

Chemicals

Soda Ash We described the sources of soda ash in our discussion of trona with the exception of a plant at Syracuse, NY owned by Allied Corp. This plant is the single remaining Solvay process soda ash plant in the U.S. It uses salt, ammonia and calcium carbonate as the feed materials. The first stage makes sodium bicarbonate. From there on it follows the same sequence as described for Kerr-McGee; light soda ash, sodium carbonate monohydrate and finally dense soda ash.

This plant is rated at 700 thousand tons per year of soda ash and so has the necessary capacity to be a supplier of bicarb, light soda ash, monohydrate or dense soda ash to the dry injection market. Allied also makes sodium sesquicarbonate but it is made in a separate plant with a relatively small capacity and so would probably not be considered a source for sorbent.

Sodium Bicarbonate We have mentioned that large volumes of sodium bicarbonate are produced by Kerr-McGee and Allied Syracuse as intermediates in soda ash production. There is an additional quantity of bicarbonate that is produced for sale.

Four producers operate a total of five plants with a combined capacity of 470 thousand tons per year. All plants begin with soda ash as the starting material and react it with carbon dioxide to form bicarb in a highly pure form. The dried and sized products are used in a variety of food, drug and feed markets.

Church and Dwight, the largest of the merchant producers of bicarb, is proposing to build bicarb plants at the utility site using CO_2 from the flue gas to do the carbonation. The economics of such a process depend heavily on the cost of starting material (soda ash) and whether an organic extraction process is required to obtain suitable CO_2 from the flue gas.

This is an intriguing concept to take advantage of the lowest transportation cost and the highest demonstrated SO_2 reactivity. However, one real drawback exists even if the economics are viable. There is the perception even if the utility does not own or operate the bicarb plant that the process is no longer simple and "non-chemical".

Sodium Sesquicarbonate This chemical sorbent was discussed in the Wyoming trona section. It is simply the refined form of trona. FMC's process to make soda ash via the sesqui process has this purified trona as an intermediate. The process is rated at 1.8 million tons per year as sesqui.

Currently, some of the sesqui is further purified to remove a trace color impurity before sale to the merchant market. As the slight color has no detrimental effect on FGD the bulk of the sesqui is available to dry and ship "as is" for dry injection scrubbing.

Other Chemicals Both monohydrate and decahydrate are made by several producers as intermediates for further processing to soda ash. Tribi is not produced in anything but research quantities. None of these have been demonstrated to be effective sorbents but were added for completeness.

Table III summarizes the materials that are produced and the capacities that exist today.

It should be apparent from the foregoing discussion that as compared to as few as three years ago, the question of whether any sorbent is available for dry injection should be put to rest. The question is now not, "What sorbent is available?" but "Which should I choose?"

DRY INJECTION COST EVALUATION

It would be appropriate to move into a discussion of sorbent characteristics and properties. However, that is important enough to be the subject of a separate paper. Instead I would like to discuss evaluation of costs and how to combine them into a comprehensive assessment of dry injection costs.

With so many possible sorbents with different properties and shipped from different locations the evaluation appears complex. Additional complications enter when trying to compare all the parts supplied individually or together as a package. If we have a mechanism to draw all the pieces into one final cost to the utility, the job is simplified. The goal is then to develop a route to a common form of total cost; levelized cost.

LEVELIZED OPERATING COST

Levelizing the cost starts with the total first year operating costs. They are escalated at the inflation rate for the life of the plant and then discounted to a present value. This total present value of all future operating costs is then spread evenly over the project life. The latter is done with the capital recovery factor.

The sorbent affects the operating costs in a number of ways. Certainly there is the F.O.B. origin price and the transportation cost plus the scrubbing efficiency which defines the volume of sorbent needed. Volume of sorbent also impacts the grinding cost and waste disposal cost.

First the pounds of inlet SO_2 generated is determined using design information on the plant size, heating rate, load factor and coal analysis.

We can now calculate the quantity of any sorbent that will be required.

$$\frac{\text{lbs sorbent}}{\text{hr}} = (\text{NSR})\left(\frac{1.65}{\text{lb } SO_2/\text{hr}}\right)\left(\frac{1}{\text{TA}}\right)$$

where: NSR = normalized stoichiometric ratio for the sorbent at the required SO_2 removal

TA = total alkalinity of sorbent (as % Na_2CO_3/100)

Because the sorbent cost is such a large percentage of the total cost of dry injection, the NSR used in the calculation is of key importance. It is appropriate to add a contingency in recognition of the risk involved. The size of this contingency for sorbent performance could vary from zero to probably 20% depending on the degree of confidence in the value for each sorbent and on the level of risk that the supplier will absorb.

Traditionally a chemical only supplier will guarantee to meet a set of physical and chemical specifications but not guarantee performance (SO_2 pick up in this case). This would place the burden of risk fully on the utility and constitute the maximum contingency case. The opposite case is a supplier that offers full performance guarantees. In such case no contingency is necessary on the utility's part.

With the volume just determined, we can arrive at the total sorbent dependent operating costs.

$$\text{Annual Sorbent operating costs} = (8760\ \text{hr}) \left(\frac{\text{ton sorbent}}{\text{hr}}\right) \left(P + T + G + W\right)$$

where: P = Price /ton of sorbent FOB origin
T = Transportation cost/ton
G = Grinding cost/ton
W = Waste disposal cost/ton

The grinding cost may not be fixed for all sorbents. Some sorbents may require higher horsepower per ton than others. As no universal index of grindability is available, relative testing must be done to quantify the differences.

All other operating costs can now be added to the sorbent costs to arrive at the total operating cost to be levelized.

The additional general costs to be added are:

- Operating labor
- Maintenance - Labor and materials
- Utilities - This is primarily power with dry injection. If grinding costs have been accounted for in the sorbent cost the power should not be included again in this category.
- Waste disposal - Fly ash only since the waste sorbent has already been counted.
- Overhead

Levelized Capital Cost

All the typical costs are incorporated into the total capital cost. They include:

- Turnkey system
- General facilities
- Engineering and overhead
- Contingency
- Escalation of capital
- Interest during construction
- Startup
- Land
- Working capital

The total capital cost is levelized by multiplying by the fixed charge rate.

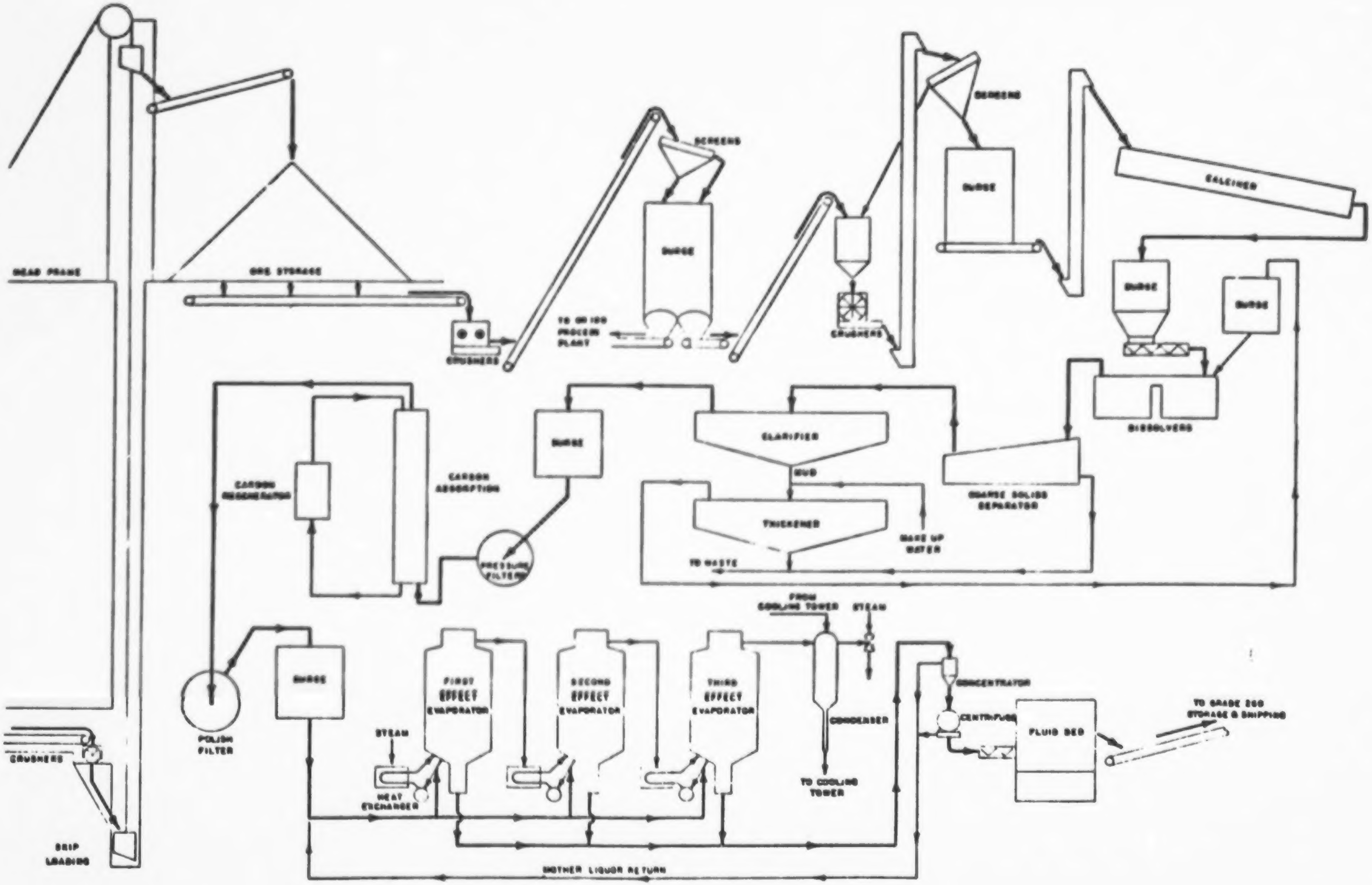
As with the discussion on contingency for sorbents, if any of these costs are covered in the suppliers offering, then they should not be counted again. If the supplier has guaranteed the system performance on SO_2 removal and availability, then the added contingency should cover only the general facilities.

Conclusions

The existing capacities to produce proven dry injection sorbents and supplier willingness to participate in this exciting new technology is more than sufficient to allow a utility to concentrate their attention on deciding which FGD system fits best, and assuming dry injection is the choice, which sorbent or which supplier has the best package.

In evaluating the suppliers' offers, the best way to assure that everything is evaluated on an equal basis and one appropriate to the utilities' need is to determine the levelized cost. All effects of various sorbents, origins, guarantees, etc will be rolled into one cost that reflects the utilities' cost for performance.

FIGURE I


HEAD FRAME
ORE STORAGE
CRUSHERS
SKIP LOADING
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SCREENS
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SURGE
SURGE
DISSOLVERS
COARSE SOLIDS SEPARATOR
CLARIFIER
MUD
THICKENER
MAKE UP WATER
TO WASTE
SURGE
CARBON REGENERATOR
CARBON ABSORPTION
PRESSURE FILTERS
POLISH FILTER
SURGE
STEAM
HEAT EXCHANGER
FIRST EFFECT EVAPORATOR
SECOND EFFECT EVAPORATOR
THIRD EFFECT EVAPORATOR
FROM COOLING TOWER
STEAM
CONDENSER
TO COOLING TOWER
CONCENTRATOR
CENTRIFUGE
FLUID BED
TO GRADE 260 STORAGE & SHIPPING
MOTHER LIQUOR RETURN

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FIGURE II

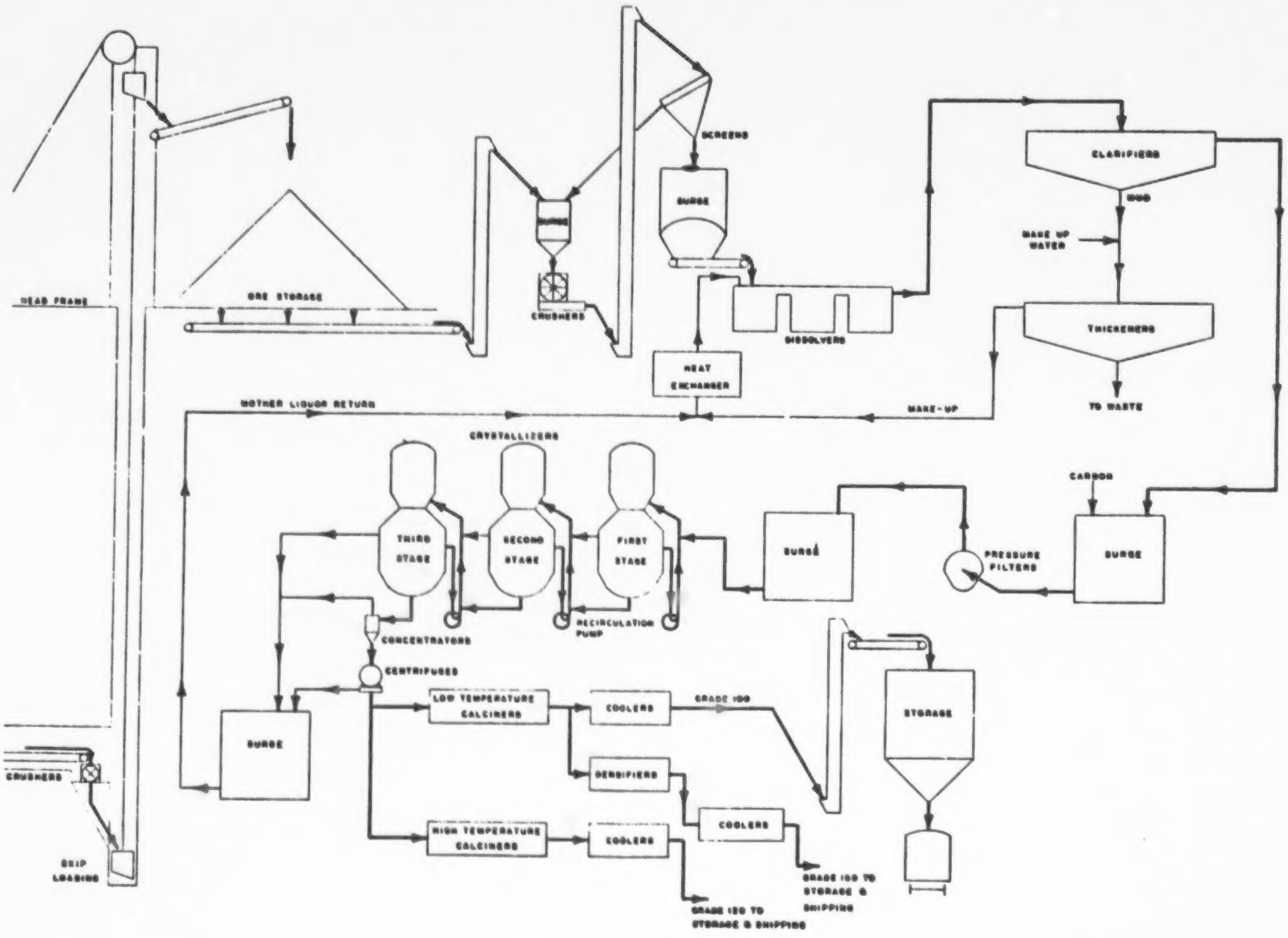
HEAD FRAME
ORE STORAGE
CRUSHERS
SCREENS
SURGE
DISSOLVERS
HEAT EXCHANGER
CLARIFIERS
MUD
MAKE UP WATER
THICKENERS
TO WASTE
MAKE-UP
MOTHER LIQUOR RETURN
CARBON
SURGE
PRESSURE FILTERS
SURGE
CRYSTALLIZERS
FIRST STAGE
SECOND STAGE
THIRD STAGE
RECIRCULATION PUMP
CONCENTRATORS
CENTRIFUGES
SURGE
LOW TEMPERATURE CALCINERS
COOLERS
GRADE 100
DENSIFIERS
COOLERS
GRADE 100 TO STORAGE & SHIPPING
HIGH TEMPERATURE CALCINERS
COOLERS
GRADE 120 TO STORAGE & SHIPPING
STORAGE
CRUSHERS
SKIP LOADING

Table I

Sodium Carbonate Chemicals

Chemical Name	Common Name	Formula	% Na_2CO_3
Sodium Carbonate	Soda Ash	Na_2CO_3	100
Sodium Sesquicarbonate	Sesqui	$Na_2CO_3+NaHCO_3+2H_2O$	70
Sodium Bicarbonate	Bicarb	$NaHCO_3$	63
Sodium Carbonate Monohydrate	Crystal Carbonate	$Na_2CO_3+H_2O$	85
Sodium Carbonate Decahydrate	Washing Soda	$Na_2CO_3+10H_2O$	37
Sodium Carbonate Trihydrogen Carbonate	Tribi	$Na_2CO_3+3NaHCO_3$	74

Table II

Sodium Carbonate Minerals

Ore	Chemical Constituent
Trona[1]	Sodium sesquicarbonate
Nahcolite[1]	Sodium bicarbonate
Wegscheiderite[2]	$Na_2CO_3.3NaHCO_3$
Natrol[1]	Sodium carbonate decahydrate
Thermonatrite[1]	Sodium carbonate monohydrate

1 Industrial Minerals and Rocks, 4th Ed.; Lefond, S.J., Ed.; Am. Inst. Mining, Met. & Pet. Eng. p 1063 (1975)

2 Fahey, J.J. et. al.; Geol. Soc. Am. Abstracts 1961 Ann. Meetings, p 48A-49A (1961)

Table III

Plant Products and Capacities[1] (MM Tons)

	Trona	Calcined Trona	Mono-hydrate	Soda Ash	Sesqui	Deca-hydrate	Bicarb
FMC, WY	5.1	1.8	1.8	2.8	1.8	0.5	-
Allied, WY	4.0	2.6	2.6	2.2	-	NA[2]	-
NY	-	-	0.8	0.7	-	-	1.1
Stauffer, WY	3.3	2.1	2.1	1.8	-	-	-
IL	-	-	-	-	-	-	0.070
Texas Gulf, WY	1.8	1.2	1.2	1.0	-	-	-
Tenneco, WY	1.8	1.2	1.2	1.0	-	-	-
Kerr-McGee, CA	NA	-	1.3	1.4	-	-	2.2
Cominco, CA	0.1	-	-	-	-	-	-
Church & Dwight, WY							0.190
OH							0.090
Riverside Prod. GA							0.020

[1] Manufacturers and industry sources: capacities are the maximum for each material but cannot all be produced at one time

[2] NA = information not available

SODIUM BICARBONATE FOR SULFUR DIOXIDE EMISSION CONTROL

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Church & Dwight Co., Inc.
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Piscataway, New Jersey 08854

ABSTRACT

It is anticipated that more and more stringent controls on SO_2 emissions from public utility and industrial coal fired boilers will be imposed. It is further recognized that wet scrubbers, spray dryers and variant systems require heavy capital investment and are troublesome to operate. The dry sodium based sorbent injection technique using a bag house for collection of fly ash and reactants is attractively simple in operation and effective. Important considerations in the selection of this technique over alternative systems are the reliable availability of sorbents and the impact of freight to allow dry injection to be competitive with alternative systems.

The focus of the paper will be on a concept to economically provide sodium bicarbonate as a sorbent to control sulfur dioxide emissions using the dry injection technique.

GENERAL COMMENTS

It is anticipated that more and more stringent controls on sulfur dioxide emissions from public utility and industrial coal fired boilers will be imposed. The nature of the legislation remains to be defined but there is little doubt that substantial reductions in emissions will be required.

Many collection systems have been tested and some implemented on major facilities. Systems which use wet lime or limestone as the scrubbing medium have generally been effective in meeting emission reductions but also have been recognized to require a heavy initial capital investment. Further, these units need significant operating and maintenance attention to assure their performance.

The developing alternative of the dry injection technique using a sodium based sorbent offers two major advantages over these wet collection systems.

1. Capital investment is a fraction of that for a wet system; about 15-20%.
2. Operation is attractively simple.

PREFERRED SORBENT

There has been an on-going evaluation of a variety of sodium based compounds for use as sorbents. Among these have been:

Commercial sodium bicarbonate
Solution mined nahcolite (98% bicarb)
Conventionally mined nahcolite (70% bicarb)
Trona from Wyoming
Trona from California
Sodium sesquicarbonate
Soda ash

In each comparative test, it has been recognized that the manufactured or mineral form of sodium bicarbonate is the most effective sorbent of the group. Recent work has indicated that the effectiveness of the sorbent can be further enhanced by reducing the particle size of the injected compound.

One of the most convincing demonstrations of effectiveness has been the work performed at the Cameo station by EPRI and reported in the spring of 1983. The following graphically presents this evaluation. These figures are used for calculations of relative quantities of each sorbent in this paper. It is recognized that the nahcolite used was conventionally mined material with about 30% inert materials and the remainder sodium bicarbonate. The identification of sodium bicarbonate as the effective sorbent is clear.

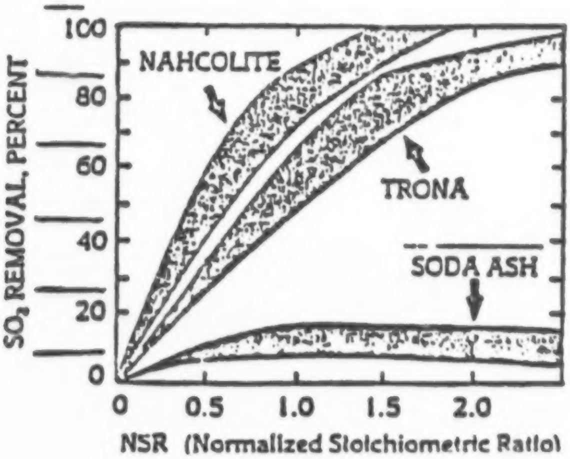

Figure 1. SO_2 Removal at Steady State as a Function of Normalized Stoichiometric Ratio

AVAILABILITY AND PRICE

Even though sodium bicarbonate has consistently demonstrated effectiveness, the price of commercially available, high quality (U.S.P.) material was prohibitively high for consideration as a sorbent; about $300/ton plus freight from established producing locations.

> NOTE: U.S.P. refers to the quality specified by the U.S. Pharmacopeia which defines assay, trace chemicals and other qualities to permit its use in foods, antacids and other products which are internally consumed.

Also, nahcolite, the mineral form of sodium bicarbonate, was not commercially available and required significant elapsed time to demonstrate its consistent availability and eventual price.

In short, a reliable source of non U.S.P. sodium bicarbonate suitable for use as a sorbent was required. And, preferably, it was to be based upon raw materials or minerals which were commercially and readily available.

CONCEPT

Against this background, a technique was conceived and technology developed to produce sodium bicarbonate at the site of a power facility. This process will use sodium carbonate, which is commercially available in large quantities, and carbon dioxide from stack gases at the power facility itself.

SOME FUNDAMENTALS

To demonstrate the attractiveness of the concept it is necessary to recognize some fundamental information. And, to do this, the standard Kenosha, Wisconsin plant with two 500 MW units burning coal with a 0.48% sulfur content has been selected for illustration.

The required removal level as dictated by the New Source Performance Standard is 70% of the sulfur dioxide in the combustion products.

Using these criteria and the Cameo data as a basis, the estimated quantities required of each of the major sorbent options then is as follows:

	Tons/Year
Trona	136,000
Sodium Sesquicarbonate	117,000
Conventionally Mined Nahcolite	112,000
Sodium Bicarbonate	79,000
solution Mined Nahcolite	79,000

However, if soda ash, the most concentrated practical form of sodium values which is commercially available, is shipped to the Wisconsin location for subsequent conversion to sodium bicarbonate on site, the quantity is reduced to:

Soda Ash for on site conversion	53,000 tons

NOTE: One ton of soda ash will be converted to approximately one and a half tons of sodium bicarbonate in the carbonation step on site using carbon dioxide from the stack gases.

FREIGHT IMPLICATIONS

Freight is a non productive cost. It is also an on-going and usually escalating cost. It is of fundamental interest to minimize freight on all materials.

Freight comparisons on the alternative sodium based sorbents can be estimated. A freight rate of $50/ton for all materials shipped from Green River, Wyoming has been assumed for this illustration and clarity. It should be recognized that the freight rate actually applied will be a result of negotiations with the railroads involved and individual rates could vary this figure by plus or minus a few dollars. Further, for nahcolite, which is in a comparatively remote location, the $50/ton rate may be lower than actual costs to load trucks, transload to hopper cars and then ship.

Nevertheless, the following chart illustrates freight implications for each:

SORBENT	QUANTITY REQUIRED	ANNUAL FREIGHT COST AT $50/T
Trona	136,000 T	$6.80MM
Sodium Sesquicarbonate	117,000	5.85
Conventionally Mined Nahcolite	112,000	5.60
Sodium Bicarbonate	79,000	3.95
Solution Mined Nahcolite	79,000	3.95
Soda Ash for on-site conversion	53,000	2.65

The carbon dioxide used in this carbonation concept is drawn from the stack gases. Therefore, there is no freight cost for the gas:

Freight on CO_2 $0

In short, movement of soda ash for on-site conversion to sodium bicarbonate will minimize unproductive and on-going freight costs.

AVAILABILITY

At this point, a comment on the availability of soda ash is appropriate. The current producers in the U.S. and their capacities (as listed by the U.S. Bureau of Mines) are as follows:

Producer	Annual Capacity
Allied	2.9MM tons
FMC	2.85
Stauffer	1.96
Kerr McGee	1.45
Tenneco	1.0
Texas Gulf	1.0
TOTAL	11.16MM tons

The production for the first six months of 1984 was 4.2MM tons or an annual rate of:

8.4MM tons

Therefore, the present capacity utilization and the additional amount available, up to capacity, is

Capacity Utilization	75%
Available Soda Ash	2.76MM tons

Further, availability is not limited to this quantity since many of the operations are expandable to meet an increased demand. In short, there is and likely will be an ample supply of soda ash to meet the demand for its conversion to sodium bicarbonate and soda ash is distributed through an extensive well established network.

In contrast, trona until recently has not been commercially available and nahcolite sources are still in development stages.

ON-SITE CARBONATION

The following simplified flow chart illustrates that following a bag house, a portion of the fly ash free gas is drawn into a unit to purify and concentrate the carbon dioxide. The carbon dioxide is combined with soda ash in a reactor to produce the sodium bicarbonate. This then is available for injection up stream from the bag house for removal of sulfur dioxide.

OTHER ATTRACTIONS

The attractions of comparatively low capital requirement for a dry injection system and its simplicity have been discussed. Burdensome freight costs can be held to a minimum by moving readily available soda ash for conversion to bicarb on-site. But, there are other attractions to the concept:

- Since fewer tons are to be handled, hopper car unloading, bins and handling equipment are proportionately reduced in size.
- Space requirements are lower.
- The sodium bicarbonate produced is comparatively fine and friable the need for high capital grinding equipment is minimized.
- There are virtually no insolubles which add to the waste load.

When considered comprehensively, these attractions are also quite compelling.

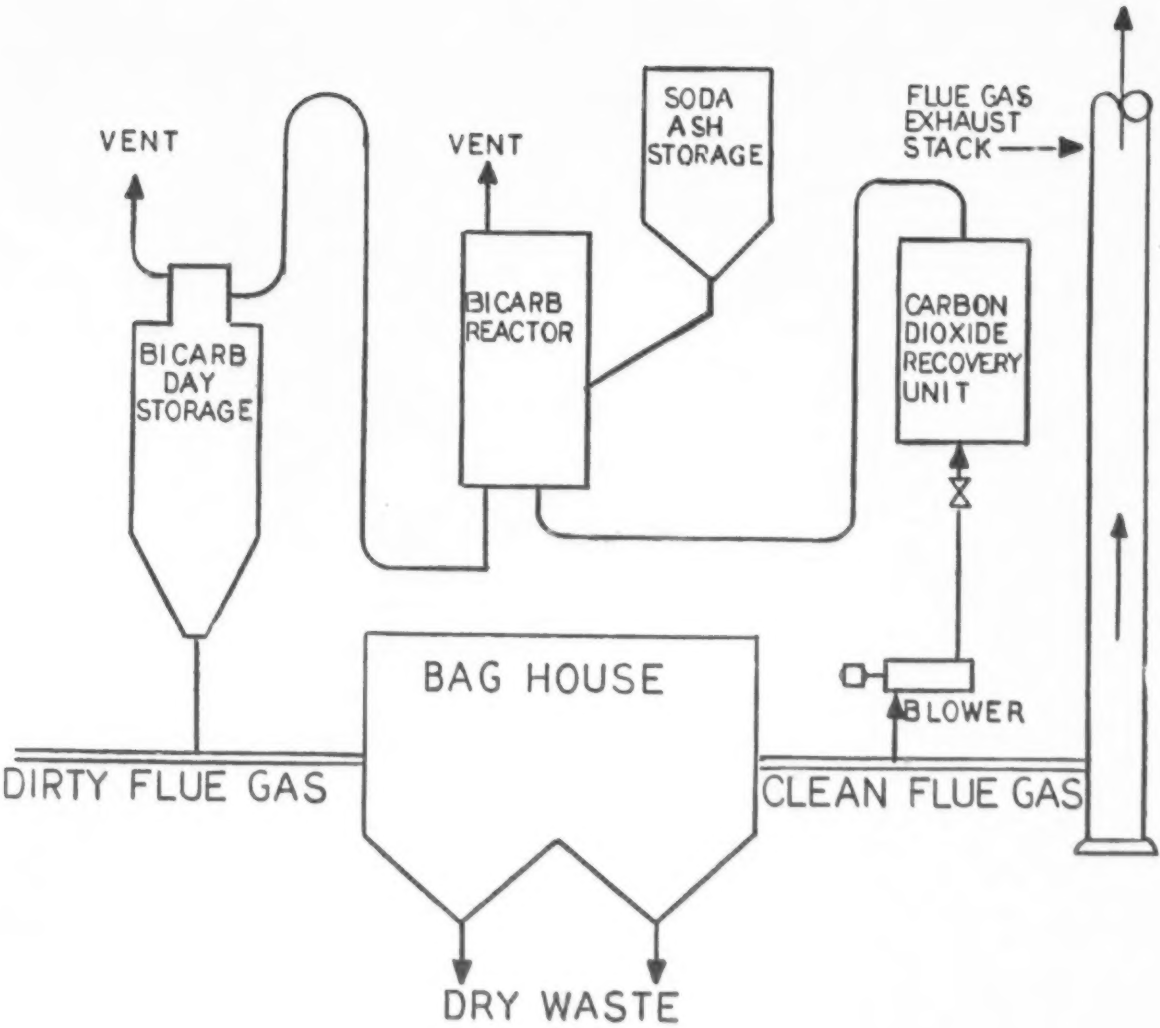
VENT
VENT
SODA ASH STORAGE
FLUE GAS EXHAUST STACK
BICARB DAY STORAGE
BICARB REACTOR
CARBON DIOXIDE RECOVERY UNIT
BAG HOUSE
BLOWER
DIRTY FLUE GAS
CLEAN FLUE GAS
DRY WASTE

Figure 2. On-site Bicarb

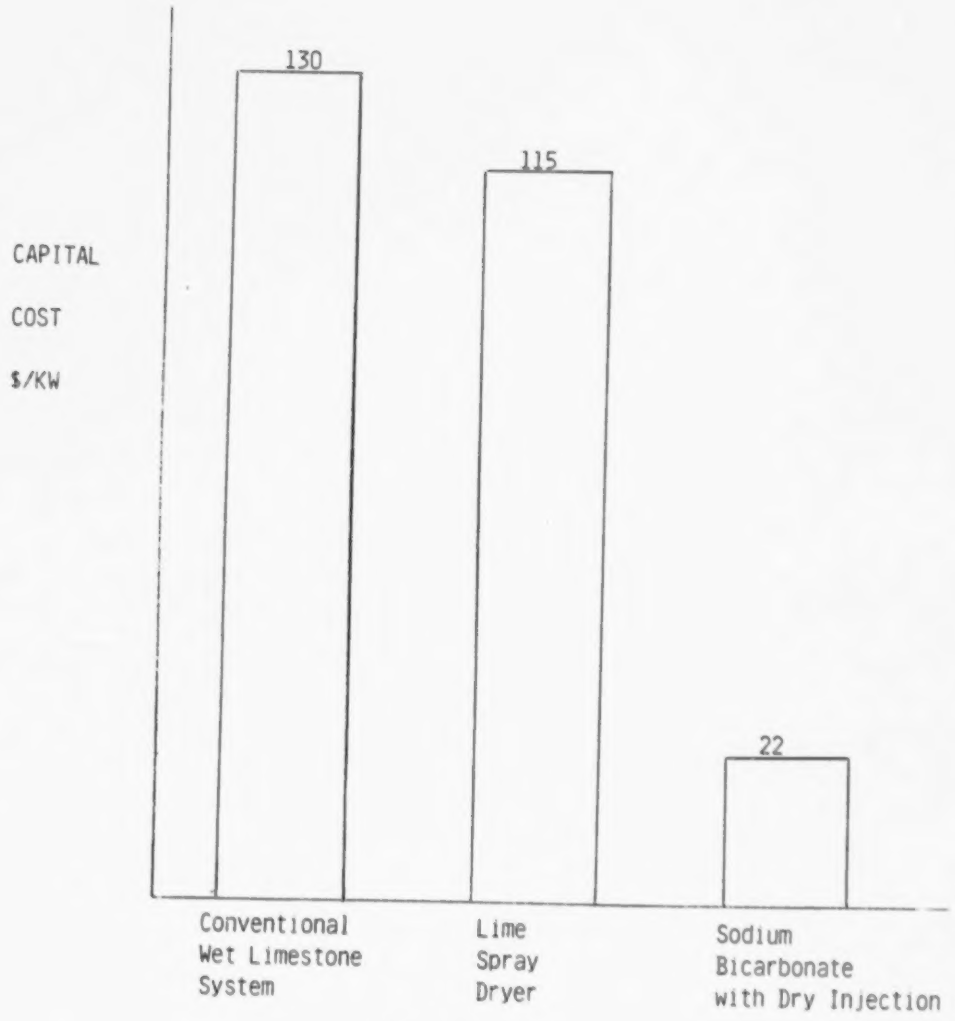
130
115
22
CAPITAL
COST
$/KW
Conventional
Wet Limestone
System
Lime
Spray
Dryer
Sodium
Bicarbonate
with Dry Injection

Figure 3.

ECONOMICS

The comparatively low capital requirement for a dry injection unit is illustrated in the following chart developed for the Kenosha facility.

Further, levelized bus bar costs for this location have been estimated. These consider freight, capital, operating and sorbent costs for the Kenosha facility.

On the basis of a 30 year project life the comparison is as follows:

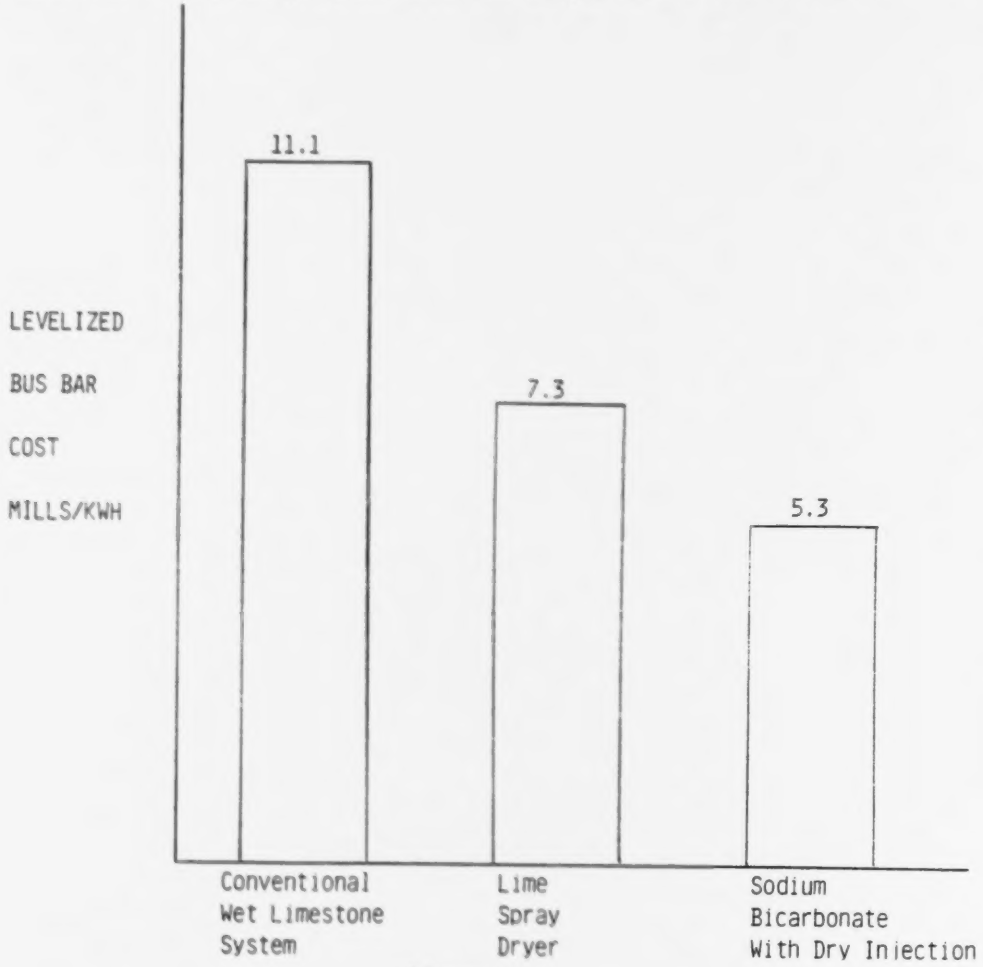

Figure 4.

A shorter project life amplifies the economic advantage of the dry injection technique using sodium bicarbonate produced on-site. To illustrate this a 15 year life of these same facilities show the following comparison.

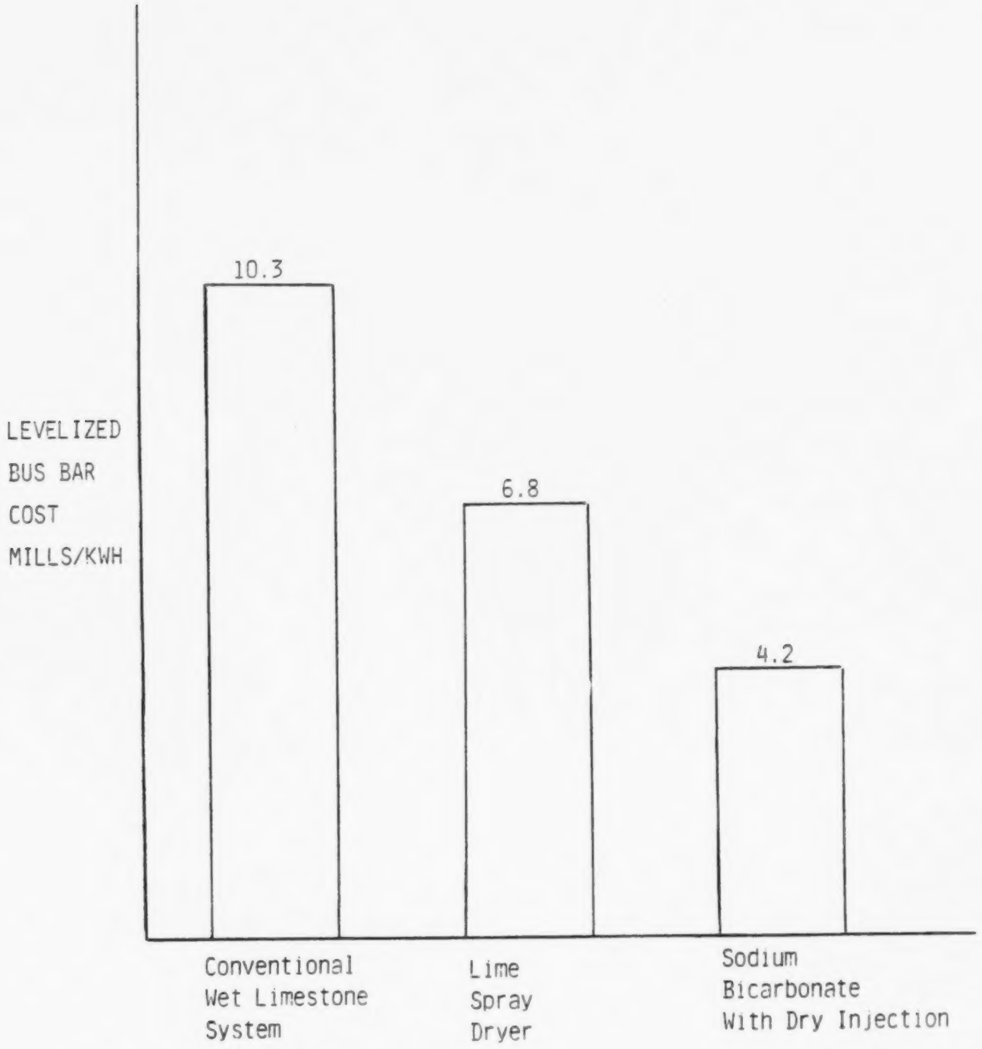
LEVELIZED
BUS BAR
COST
MILLS/KWH
10.3
6.8
4.2
Conventional Wet Limestone System
Lime Spray Dryer
Sodium Bicarbonate With Dry Injection

Figure 5.

The attractions to dry injection and to on-site preparation of sodium bicarbonate are substantial.

SUMMARY

It is recognized that each power facility has its individual design criteria. Coal quality, geography, size, retrofit options and many other factors will influence selection of collection techniques. Each location must, therefore, be independently analyzed.

In summary, however, a technique has been conceived and a technology developed which permits preparation of the preferred dry sorbent, sodium bicarbonate, at the site of a power facility. This technique will strongly support the dry sorbent injection alternative to control SO_2 emissions and enhance its fundamental attractions of reduced capital and simplicity of operation.

SESSION VIII: FIELD APPLICATIONS AND FULL-SCALE TESTING

Chairman, Richard Stern, EPA, IERL/RTP

REDUCTION OF SO_2-EMISSION IN BROWN COAL COMBUSTION; RESULTS FROM RESEARCH AND LARGE SCALE DEMONSTRATION

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ABSTRACT

For more than 10 years the Rheinisch-Westfälisches Elektrizitätswerk (RWE), Germany's largest utility company was involved in the development of the Dry Additive Process (DAP) for SO_2 removal by utilizing dry calcium based materials. Based upon results from trials at a combustion rig and a 60 MW utility boiler a full scale demonstration plant at a 300 MWe brown coal boiler was installed.

During a more than one years' program at this installation the reduction of SO_2-emission, the maximum possible amount of additives with regard to operational behaviour of various power station components and different injection modes have been investigated. The large scale operation was accompanied by rig tests concerned with the application of CaO-rich ashes from different preparation procedures.

The paper deals, apart from the major results for SO_2-reduction of the three different test scales, with various operational problems associated with the additive injection and discusses the experience with practial solutions.

INTRODUCTION

During the last decade an increased utilization of solid fossil fuels in large scale heat and steam generation facilities (particularly in electricity production) was observed. This tendency was especially well pronounced in countries which contain coals of different ranks, which - up to a recent date - were not competitive with cheaper imported fuels.

During the same period of time, environmental considerations in industrial and utility combustion became a major concern; these concerns were expressed by the adoption of clean air acts in several countries. Therefore, industry was forced to reduce and maintain certain concentrations of discharged solid and gaseous matter in flue gases below a maximum concentration allowed, set forth in the clean air acts. Among the noxious gases, sulfur oxides are of major importance; they become available as combustion products from sulfur which is bound organically within the fuel as a mineral impurity.

The techniques for reduction of sulfur oxide emission are, in principle, known and in many cases are used on present combustion systems. In general, there are various methods applicable:

- fuel selection and blending
- sulfur removal prior to combustion
- wet flue gas cleaning
- retention of sulfur oxides during or after combustion by dry sorbents.

The first two methods can be only applied under certain site specific conditions, and are in most cases technically and/or economically efficient if stringent emission limitations are set by performance standards. Wet flue gas cleaning, however, is at date a known technique and SO_2 scrubbing systems are installed e. g. behind oil, bituminous, and subbituminous coal fired boilers.

Experience with coal fired units is, with restrictions, positive; but this may not be necessarily transferable to systems burning other fossil fuels, e.g. low rank fuels like brown coals. Also, phenomenological, technical, or economical considerations very often show that the installation of scrubbing systems may not be the most appropriate solution. This is particularly true if existing power stations must be retrofitted with SO_2-removal devices. In the above cases, the application of processes using dry sorbents, which may be blended with the fuel or injected either into the combustion chamber or the flue gas duct, offer major advantages.

BASIC CONSIDERATIONS

During combustion the sulfur content of the fuel is converted primarily to SO_2. The subsequent oxidation to SO_3 is kinetically limited and,therefore, its concentration is small in most cases. For solid fuels with high concentration of basic components, like coals from the Rhinish basin in the Federal Republic of Germany a high percentage of the SO_2 is retained in the fly ash in the form of solid sulfates. It is believed that a catalytic surface reaction

$$MO + SO_2 + 1/2\ O_2 \quad MSO_4 \longrightarrow (M = \text{basic metal})$$

is responsible for the sulfation process. This "natural retention" is a heterogenous reaction which is not only dependent upon the local temperature and concentration of the reactants and their products, but also upon the mixing of the species and the available surface area of the solid component. Since the thermodynamic equilibrium conditions are not attained in practical combustion systems, the residence time must also be considered. The sulfation process described above can be used for further SO_2 removal if a basic oxide is added to the fuel or the combustion products. The residence time available in the necessary temperature range for sulfation is limited, and therefore a high specific surface area of the solid additive and optimal mixing of the additive with SO_2 are vital conditions.

SPECIFIC PROPERTIES OF RHINISH BROWN COALS

In the Federal Republic of Germany the brown coal from the Rhinish basin is one of the importantprimary energy sources with an annual mine production of 120 million tons. 100 million tons of these are burnt in power stations to generate almost 30 % of the total public electricity demand in the country.This fuel differs from other solid fossil fuels (e.g. bituminous coals) in many respects. The high moisture content of 55 - 62 % leads not only to a considerable flue gas volume but also limits the maximum flame temperature not to exceed 1150 °C. Also the high specific fuel consumption of 1.1 - 1.4 tons/MWh, approximately 3 to 4 times higher than for German bituminous coals, prevent sufficient blending which would be necessary to guarantee a reasonably homogeneous fuel composition. Consequently the utilities are faced with a large and unpredictable variation of fuel properties. Typical fluctuations based on shift averages for the two important components Ca and S are shown in Figure 1; similar variations can be expected - and are supported by measurements - on a smaller time scale. As a result SO_2 emission from boilers will also vary unpredictably over time. The stack values (shift averages) in Figure 2 show this for 4 boilers. It is noticeable that with a similar fuel composition the different installations produce absolute SO_2 emissions which differ strongly. Obviously the "natural SO_2 retention" is dependent on the local boundary conditions, in particular the time/temperature history of the sulfation process in the combustion chamber. Values of the "natural retention", defined as given in the Appendix, between 20 and 60 % are experienced /1/.

DRY ADDITIVE PROCESS TEST RESULTS

Based on the favourable effect of the "natural SO_2-retention" and with the intention to further reduce the SO_2 emission as required the Rheinisch-Westfälisches Elektrizitätswerk AG (RWE) initiated test work as early as 1974 in a combustion test facility (0,5 - 1 MW thermal capacity). Major reasons for choosing the dry additive process (DAP) for SO_2 removal from flue gases were that the typical combustion conditions in brown coal firing systems favored the sulfation process, at that time wet FGD systems showed major operational problems, and in particular, no experience was available for fuels with strongly variable sulfur contents. The results of the test work /2/ are summarized in Figure 3, which shows qualitatively the dependence of the sulfation reaction upon main combustion parameters as well as properties of the sorbents. Eventually, an optimal temperature range with regard to calcium sulfate formation was found somewhere between 600 and 1000 °C. In order to illustrate the proposed layer-type reaction, Figure 4 shows a scanning microscope analysis of an additive particle after its passage through a brown coal fired combustion chamber. While the element calcium is evenly distributed over the total cross-section indicating the particle being of additive origin (Figure 4C), the distribution of sulfur (Figure 4B) shows an enrichment at the outer edges. This indicates that the SO_2 is clearly concentrated at the particle surface. This result is further emphasized by the line scan analysis of sulfur across the white center line (Figure 4A), which shows sulfur peaks on either side of the particle.

Also by electron microscope analysis the structural changes of e.g. hydroxide subjected to different temperatures can be clearly shown (Figure 5). In a gaseous surrounding with a temperature of 500 °C (Figure 5A) the original crystal structure of the additive, indicated by the sharp edges of the material, is still visible. When heated up to 1100 °C (Figure 5B) the single particles are strongly interlinked and their outer surfaces show a rounded shape which obviously results in a reduction of the specific surface area. Further heating up to 1350 °C (Figure 5C) results in a much stronger inter-connection between the particle and an additional strong decrease of the available surface for reaction. This decay of surface area at elevated temperatures, known as "deadburning" of the additive was already shown elsewhere /3/ by measurements of specific surface areas for various materials. It also was proven (Figure 6) that any variation of the temperature in the combustion chamber, expressed either as the maximum flame temperature T_{max} or the chamber exit temperature T_{exit}, greatly influences the SO_2-retention. Furthermore the SO_2-partial pressure prior to sorbent utilization which, in turn, is strongly related to the sulfur content of the fuel and the Ca-based natural retention, is a vital driving force for the sulfation reaction when sorbents are applied (Figure 7). Additional detailed investigations on almost 70 different additives also revealed /4,5/ that type, origin, and preparation of the sorbents may substantially affect the SO_2 removal efficiency.

LARGE SCALE DEMONSTRATION EXPERIENCE

Based upon the described small scale results, a utility boiler with a capacity of 60 MWe was equipped with an additive feed and distribution system in order to investigate the dry additive process under operating conditions. The results gained at this boiler during detailed long term testing from 1977 up to 1979 were very promising /2/, leading to the decision of a full scale demonstration at a 300 MWe boiler. The installation was erected in 1982 and a full year trial operation followed in 1983. Since January 1984 this boiler is run on base load operation with constant sorbent addition of 3 % pulverized limestone fed to the raw coal prior to the mill. The large scale demonstration project follows the general scheme which is shown in Figure 8. The additive is delivered to the site by rail transport and is fed via storage bunkers and distribution vessels, such as screw feeders or similar conveying systems, to the coal feeder which supplied the coal to the mill. Both coal and additive are intimately mixed when passing through the mill and the mixture is then transported to the burner. The calcination of $CaCO_3$ or the dehydration of $Ca(OH)_2$, both resulting in free lime, and the subsequent calcium sulfate formation takes place within the boiler. The product together with the fly ash, is finally removed from the flue gases by the electrostatic precipitator.

The trials were subdivided into several series burning a large variety of brown coals with different compositions, in particular strong variations of sulfur and calcium. Also various sorbents from different origins including on site prepared hydroxides were tested. Some typical results are given in the following figures. Figure 9, left, proves (although some scatter exists) that SO_2 emission after natural retention is a function of the sulfur in the coal. The SO_2 removed by natural retention alone (Figure 9, right) can be as high as 2500 mg/m³; the increasing tendency with increasing sulfur content of the fuel is expected. Consequently fairly high values for the retention efficiency and the utilization of the calcium is the coal are calculated (Figure 10).

If the SO_2-removal by Ca is plotted (Figure 11), the expected increase with both $Ca(OH)_2$ and $CaCO_3$ is shown, although the hydrate is more effective leading to a steeper gradient. The strong scatter is typical for large scale operation, major reasons are the time dependent fluctuations of the fuel composition and the operation boundary conditions. The calculated Ca-utilization (Figure 12) for both the additives is - within limits - fairly constant over the range of sulfur in the fuel investigated. The fairly low values are mainly due to the fact that the demonstration boiler had peak temperatures above 1200 °C, which is higher than the average when burning this fuel.

Parallel with the demonstration tests, comparative short term measurements of various other brown coal fired boilers with a constant sorbent addition of 3 % $CaCO_3$ to the fuel were carried out. Figure 13 shows - apart from the scatter - that again the dependence of the SO_2 emission on the sulfur in the fuel is obvious. The calculated difference of the regression curves with and without sorbent addition, $\Delta\ SO_2$, also shows this tendency. Finally, Figure 14 compares these SO_2-removals (3 % $CaCO_3$) for 4 different power stations when the same sorbent type and percentage was applied. It can be clearly seen that site dependent variations in operational parameters will lead to different emission reductions and that variations up to 100 % for the same sulfur content in the fuel can be experienced.

INFLUENCE ON COMBUSTION SYSTEM OPERATION

During the long term tests several effects of the DAP on operation were observed. In large boilers the heat transfer pattern will change due to the more opaque atmosphere in the combustion chamber. This results in a shift of the main temperature profile into the downstream direction. Typically, Figure 15 shows the variation of the heat received by the various heat exchange surfaces. 100 % being the case without any sorbent addition the change with increasing additive percentage - the values for 4 % and 10 % $CaCO_3$ to the fuel are given - is obvious. Also a slight increase of the flue gas exit temperature of 5 to 10 °C downstream of the air preheater was observed.

An increased deposit formation is also unavoidable but can be dealt with by the installed water - and steam-fed blowing devices. Only in high temperature areas problems due to fast sintering of the deposits may ask for more attention, particularly on long term operation. In addition the air pre-heater tends to foul more rapidly, but cleaning was even after 7000 hours of operation not yet necessary.

Extensive grid measurements of the dust loading of the flue gas before and after the electrostatic precipitator had shown that for the demonstration plant no decrease of the precipitation efficiency occurred. However, an increase of the voltage by up to 10 % above the normal operation value without sorbent injection was observed after several days of high sorbent addition rates (> 10 % relative to the coal). Also with some precipitators of older design an increased occurrence of field breakdown was observed. With variable sorbent percentage a recovery effect was noticeable when the sorbent amount was reduced. A detailed observation of the plattens revealed the build-up of a deposit layer which even by enhanced rapping cycles was not removed completely.

The most problematic effect of the DAP was found in the ash handling system. The high concentration of free CaO in the ash tends to hydrate immediately in the presence of water. This not only leads to time dependent hardening of the ash during transport but also results in steam formation of any remaining water due to the exothermic hydration reaction. Consequently in-housed ash handling and transportation systems are endangered by water vapor condensation and subsequent corrosion. This problem can be only solved by temperature controlled hydration of the total ash prior to handling for disposal or further utilization.

Based on the positive results of the SO_2-emission reduction from the large scale demonstration and under careful consideration of the observed effects on the boiler performance continuous operation of this 300 MW base load unit with 3 % $CaCO_3$ addition to the fuel flow commenced in January 1984. Between fall 1985 and the end of 1986 a further 2600 MW (2 x 300 MW, 12 x 150 MW, 2 x 100 MW) will be installed with the dry additive process bringing the capacity of boilers firing Rhinish brown coals and equipped with the dry additive process for SO_2-reduction up to a total of 2900 MW.

REFERENCES

/1/ K. Hein, W. Glaser; Proceedings of the 11th Lignite Symposium, June 15-17, 1981, San Antonio, Texas.

/2/ K. Hein and A. Schiffers; BWK 31 (1979) 10, p. 389

/3/ K. Hein, W. Glaser; 6th Members Conference of the International Flame Research Foundation, May 12-14, 1980; IJmuiden, The Netherlands

/4/ W. Glaser, K. Hein and G. Kirchen; 7th Members Conference of the International Flame Research Foundation, May 9-11, 1983, IJmuiden, The Netherlands

/5/ W. Hlubek, K. Hein; VGB 63 (1983) 4, p. 327

APPENDIX

1. Natural SO_2 Retention Efficiency:

$$\varepsilon_k = \frac{SO_{2\,max} - SO_{2\,K}}{SO_{2\,max}}$$

with $SO_{2\,max}$ = theoretical maximum SO_2 concentration if all sulfur in fuel were converted

$SO_{2\,K}$ = actual SO_2 concentration prior to sorbent addition

2. SO_2 Removal by Sorbents:

$$\Delta\, SO_2 = SO_{2\,K} - SO_{2\,A}$$

with $SO_{2\,A}$ = SO_2 concentration after sorbent addition

3. SO_2 Retention by Sorbents:

$$\varepsilon_A = \frac{\Delta\, SO_2}{SO_{2\,K}}$$

4. Ca-Utilization:

$$\eta_i = \frac{\text{Ca reacted to } CaSO_4}{\text{total Ca available}}$$

Index i: K for Ca in coal only
A for Ca in sorbent only

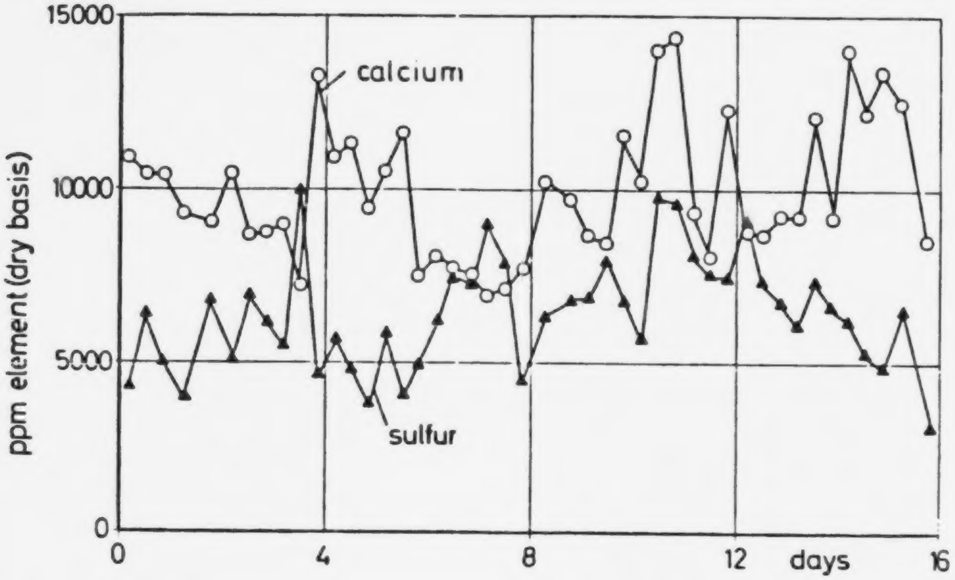


Figure 1. Boiler fuels; 8-hour average analysis

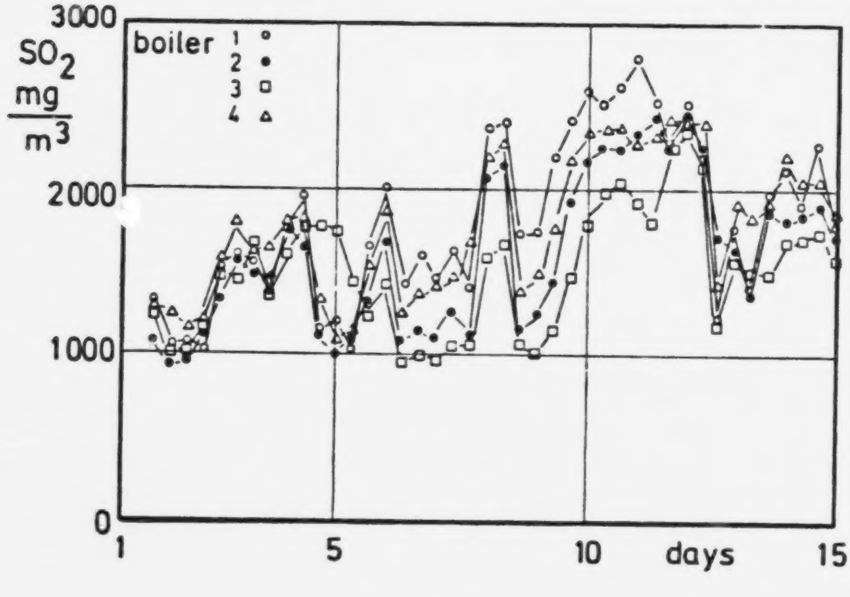


Figure 2. SO_2-emission for different boilers, shift average values (example)

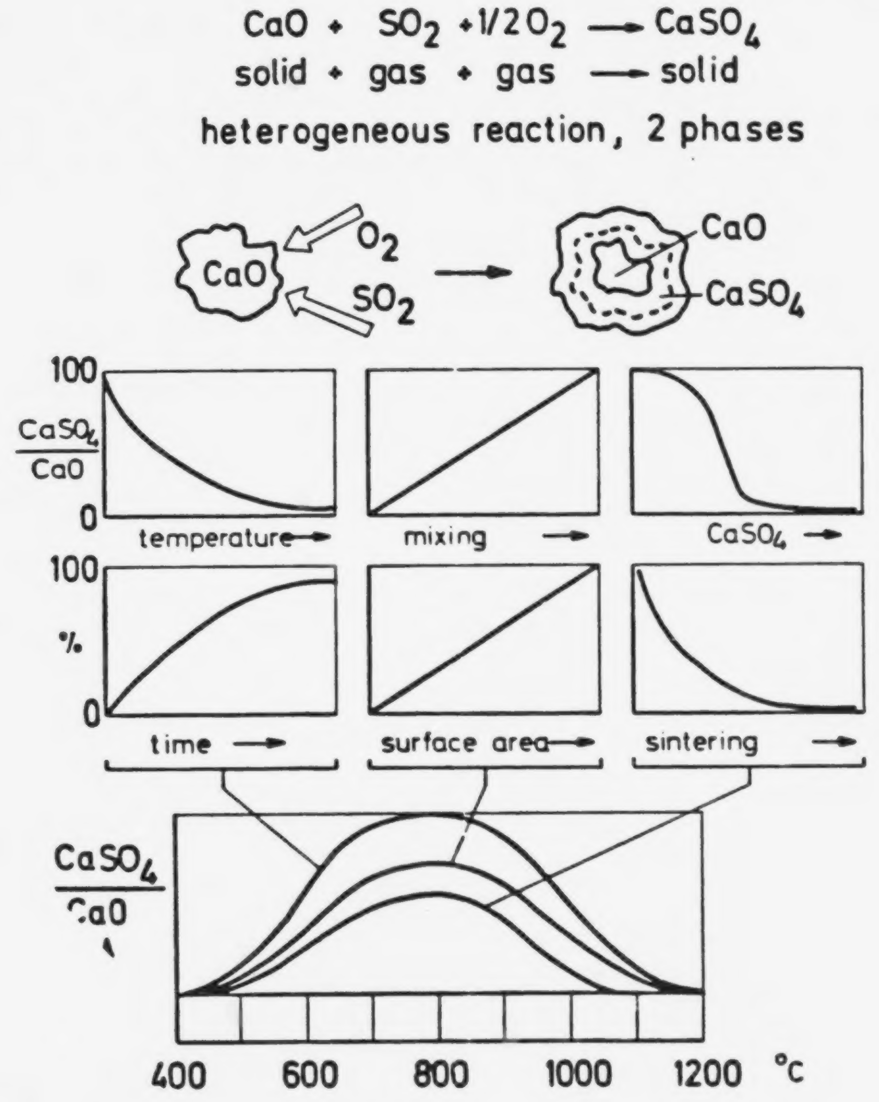

CaO + SO2 + 1/2 O2 → CaSO4
solid + gas + gas → solid
heterogeneous reaction, 2 phases
CaO
O2
SO2
CaO
CaSO4
100
CaSO4 / CaO
0
temperature →
mixing →
CaSO4 →
100
%
0
time →
surface area →
sintering →
CaSO4 / CaO
400
600
800
1000
1200
°C

Figure 3. Sulfate reaction dependencies (schematic)

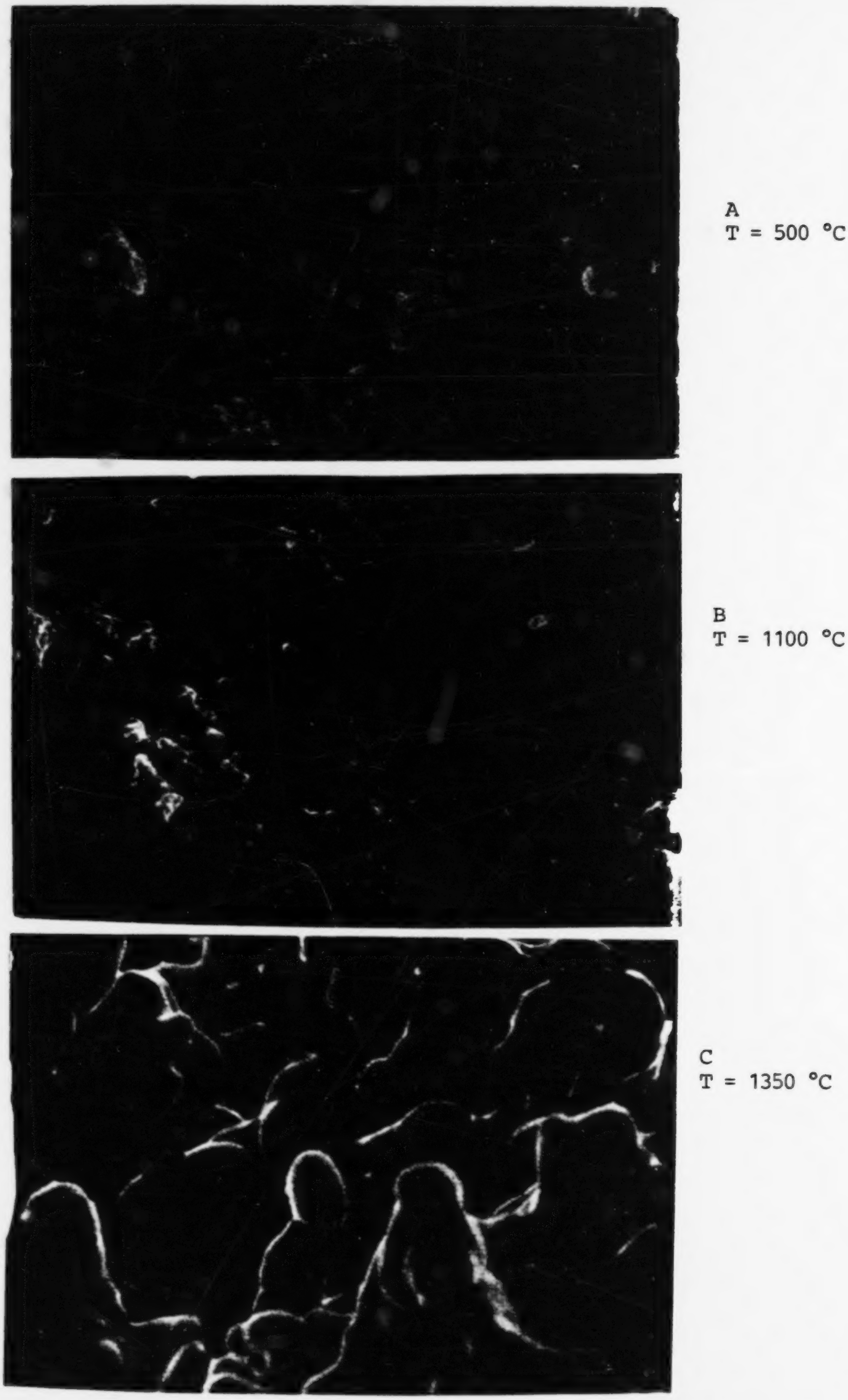
Reproduced from
best available copy.

A: Image of particle and line scan of sulfur across the particle along the white center line

B: Distribution of sulfur

C: Distribution of calcium

Fig. 4: Scanning microscopic analysis of an additive particle after having passed through the flame zone (1 cm ≙ 6 µm



A
T = 500 °C

B
T = 1100 °C

C
T = 1350 °C

Fig. 5: Ca(OH)$_2$, subjected to different temperatures (1 cm ≙ 2,5 µm)

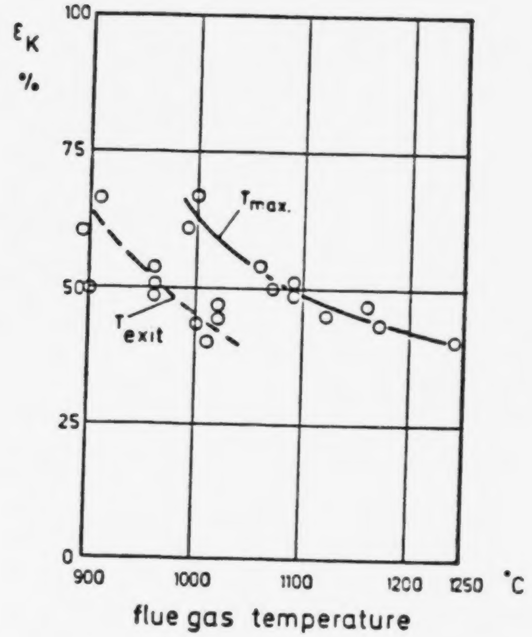


Figure 6. Natural retention and temperature

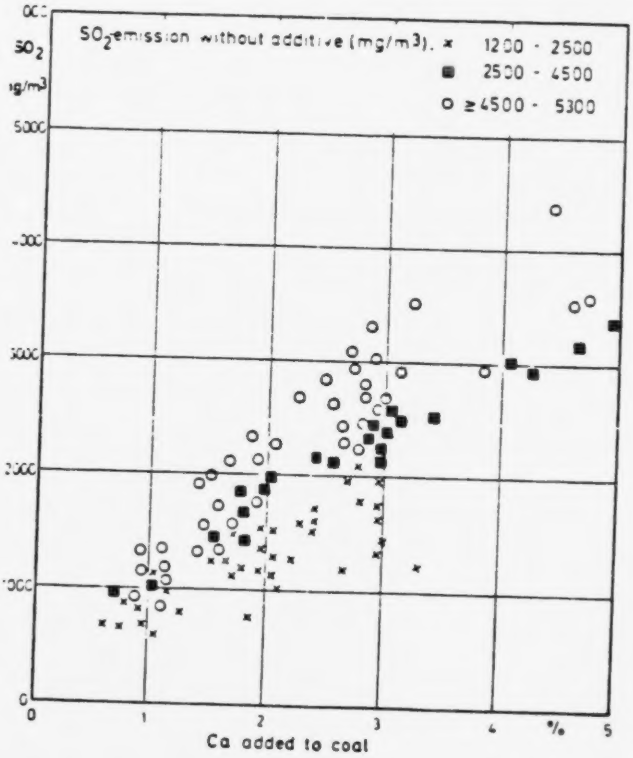


Figure 7. SO_2-removal for different coals

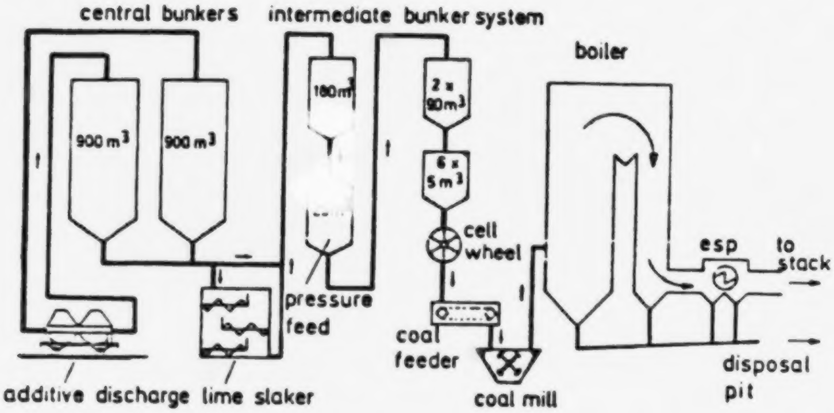

central bunkers
intermediate bunker system
boiler
900 m³
900 m³
180 m³
2 x 90 m³
6 x 5 m³
cell wheel
esp
to stack
pressure feed
coal feeder
coal mill
disposal pit
additive discharge
lime slaker

Figure 8. Demonstration Plant 300 MWe (scheme)

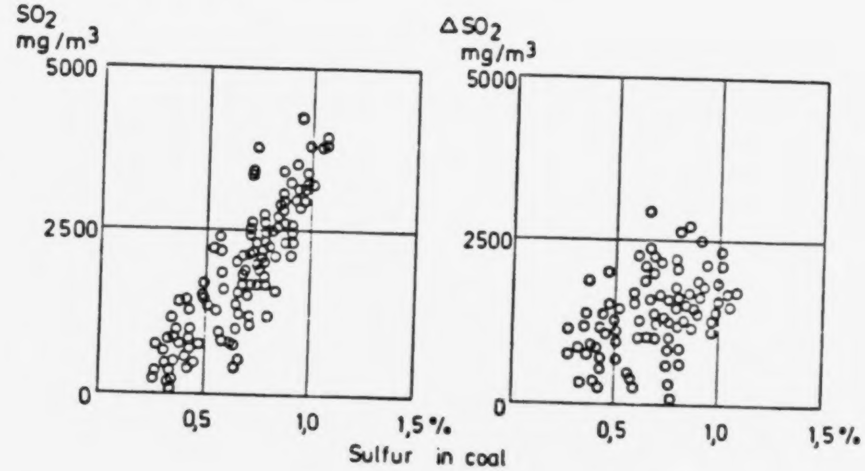


Figure 9. SO_2-emission and natural retention Δ SO_2

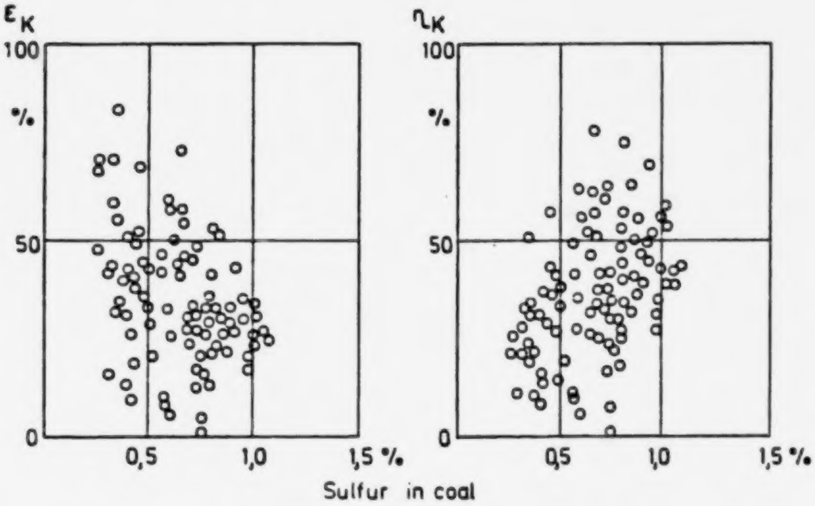


Figure 10. SO_2-retention and Ca-utilisation

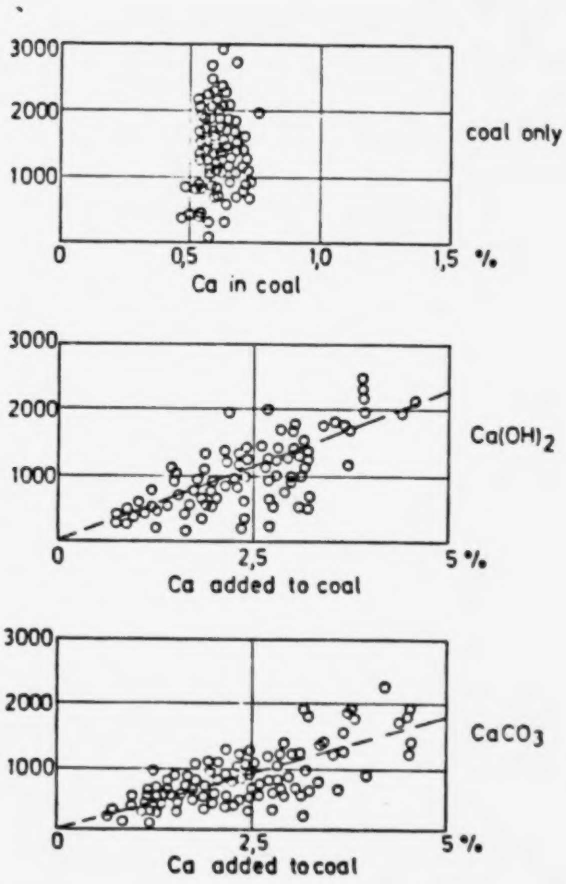


Figure 11. SO_2-removal by calcium

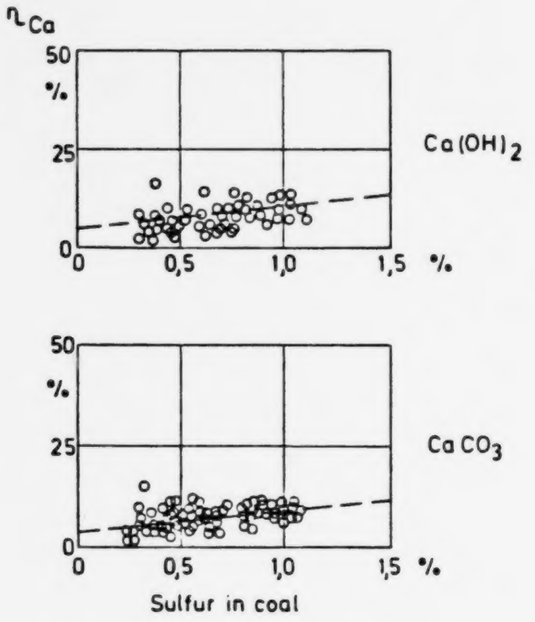


Figure 12. Utilisation of calcium

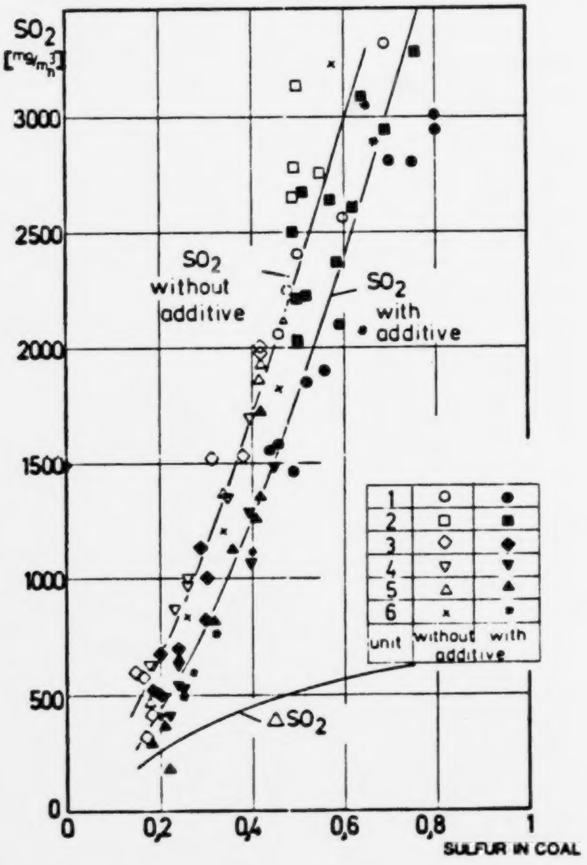
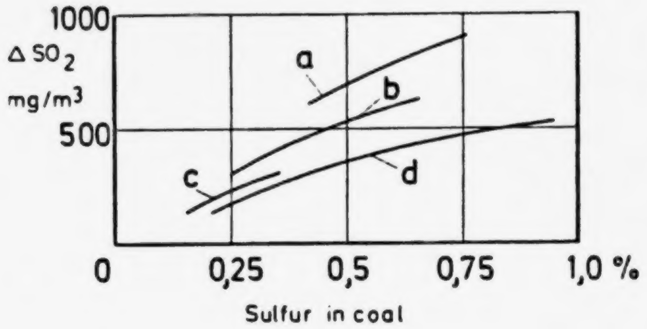


Figure 13. SO_2-emission from different boilers



Station a: 1 boiler, long term tests

Station b: 6 boilers, short term tests

Station c: 6 boilers, short term tests

Station d: 1 boiler, long term tests

Figure 14. SO_2-removal by 3 % $CaCO_3$ to coal

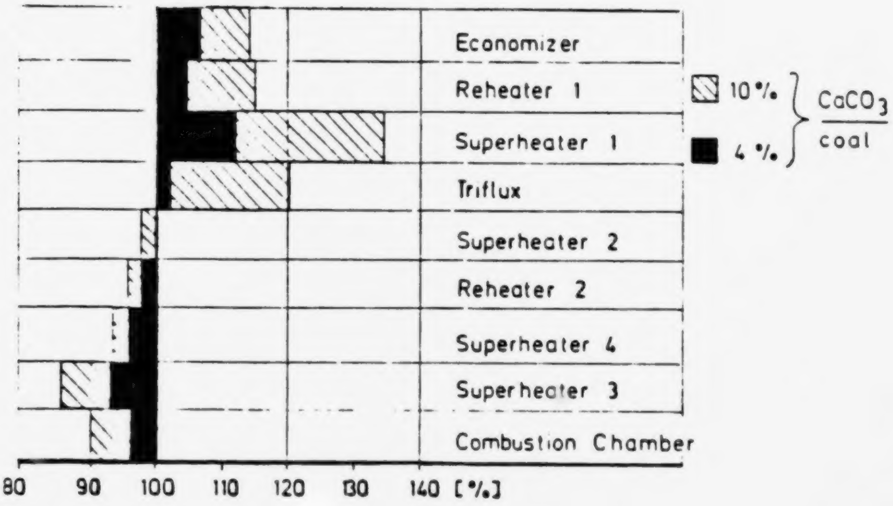


Figure 15. Variation of heat absorption

REDUCTION OF SO_2 EMISSIONS FROM A COAL FIRED POWER STATION BY DIRECT INJECTION OF CALCIUM SORBENTS IN FURNACE

H. BRICE(a), G. CHELU(b), G. FLAMENT(b), R. MANHAVAL(c), M. VANDYCKE(d)

(a) Charbonnages de France, Houillères de Lorraine
(b) Charbonnages de France, CERCHAR
(c) Charbonnages de France, Houillères de Provence
(d) Stein Industrie

ABSTRACT

HOUILLERES de PROVENCE, a company of the Nationalized Group "CHARBONNAGES de FRANCE" has conducted a trial series in a 50 MWe power station in GARDANNE (south of France) in order to evaluate the feasibility of applying the direct SO_2 capture in flames by dry calcium sorbents injection to a newly built 600 MWe unit.

This campaign of measurements on the 50 MWe boiler followed a preliminary study that had been subcontracted to the International Flame Research Foundation (Ijmuiden) in 1982 and where effects of sorbent quality, sorbent injection location, flame temperature and flue gas recirculation upon efficiency of SO_2 capture had been determined.

The experiments have indicated similar trends on the 50 MWe boiler as on pilot scale except for flue gas recycling which was effective in improving SO_2 capture in the pilot scale experiments but had no effect on the boiler.

On the boiler it was found that natural retention of sulphur in the calcium rich ash followed similar trends as retention by injected calcium carbonate ; more than 50 % SO_2 removal could be obtained with Ca/S = 3. $Ca(OH)_2$ was a much more efficient sorbent and 60 % SO_2 removal could be obtained with some $Ca(OH)_2$ injection and a high ash coal at a total Ca/S = 3 (2.4 for the ash and 0.6 for $Ca(OH)_2$).

Injection of sorbents above the upper burners elevation gave the best results.

The results of the 50 MWe tangentially fired boiler have been used to design the modifications required for applying the technique to the 600 MWe boiler which has just started operating.

REDUCTION OF SO_2 EMISSIONS FROM A COAL FIRED POWER STATION BY DIRECT INJECTION OF CALCIUM SORBENTS IN FURNACE

INTRODUCTION

The Gardanne Coal

The coal considered here is produced, at a place called GARDANNE, located in PROVENCE, about 30 km north of MARSEILLE, in the south of FRANCE. The coal is mined by HOUILLERES de PROVENCE, a company of the Nationalized Group "CHARBONNAGES de FRANCE". The output of the mine amounts to about 1.5 million tons per year and a large fraction of it is used for electricity production in a power station owned by Houillères de Provence and located at the same place. The rest (about 300 000 t) is cleaned to around 8 % ash and is used by the local industry.

Although mined underground the seams are thick and regular which allows a high productivity -about double the average productivity in the country-. Moreover the reserves are quite large (70 millions tons in the field under production plus another field of 100 millions tons) and on the whole the mining activity in this area has the potential to be economically viable for many years.

Unfortunately the GARDANNE coal contains a lot of sulphur. Table 1 gives analyses of three qualities of the coal. The washed coal is used in industry but the power station burns high ash coals.

The "base coal" which was considered for the boiler design has 12 % moisture, 22.8 % ash and 4.1 % sulphur. However the ash content varies and can be up to 35 % although the fuel actually being sent to the boiler is usually below 30 % ash ("high ash coal" in Table 1). The GARDANNE coal can be qualified as a sub--bituminous coal but is close to a bituminous one. It has a high volatile matter content - 38 % on raw coal but the coal minerals, being very rich in calcium carbonate, a significant amount of the volatile matter is CO_2 coming from the decomposition of carbonates : between 9 % and 14 % of the coal weight.

This high calcium content is a peculiar and interesting feature of the GARDANNE coal. Figure 1 shows that when a range of coals having variable ash content is considered, the CaO content in the ash is not constant but tends to increase strongly with the ash content. If one considers the washed coal as one extreme of the spectrum, it is very low in calcium. This result comes from the fact that calcium is present in the coal minerals in the form of large inclusions of $CaCO_3$ which are easily removable from the organic matrix. These inclusions can be from a few milimeters in size up to real banks of a few meters length in the coal seams.

On the whole, as illustrated in Figure 1, the molar Ca/S ratio of the raw coal is in the range 1.5 to 3 which provides an interesting potential for natural retention of sulphur in the ash.

The Provence power station

The power station is now made of 5 units :

- three 50/60 MWe units were built in the fifties
- one 250 MWe unit was built in the early seventies
- one 600 MWe unit which was commissioned in October 1984.

The first unit was built by Stein-Alsthom and is tangentially fired. The new 600 MW unit is also tangentially fired and has been constructed by STEIN-INDUSTRIE whilst the three other units are wall-fired. As the 600 MWe unit has been put in operation, this unit and the 250 MWe unit will ensure the electricity production and the three 50 MW units are in the process of being shut down.

The environment

There is presently no general regulation in France concerning SO_2 emissions but in most places and particularly in industrial and urban areas, SO_2 concentrations on the ground are continously measured at numerous locations which are known to be critically exposed to pollutant falls. When these measurements indicate too high concentrations, the usually well known SO_2 emitters are urged to reduce their emissions by reducing outputs or by burning low sulphur fuels.

The urban area around MARSEILLE is particularly protected in this way due to the presence of a number of large industries (oil refineries, iron and steel industries, power station. etc...) which are known to be SO_2 emitters.

There is also, for the city of MARSEILLE, a local regulation limiting the SO_2 emissions to 0.58 g/MJ (equivalent 2.4 g/10^6kcal or 1.32 lb/10^6Btu). Thus there has been, before and during the construction of the 600 MW unit a strong local pressure towards a significant reduction of the local impact of SO_2 emissions from this new unit of the power station. A first answer to the concern was the erection of a 300 m high chimney in order to improve the pollutant dispersion. The main effect of this very high chimney was to attract further attention of people to the subject which resulted in some more pressure to actually reduce SO_2 output. In 1981 Charbonnages de France studied the possibility of setting up an F.G.D. system for the 600 MW unit but it was concluded that this solution would deteriorate to an unacceptable level the profitability of the power station and consequently of the mining activity itself.

Therefore, in April 1982, Charbonnages de France opted for direct SO_2 capture. The objective was then to improve the natural retention if possible and to inject supplementary sorbent in order to achieve 60 % SO_2 capture at a much lower cost. This option was considered to be an acceptable compromise between environmental and economical demands. A research and development programme was then initiated in order to test and demonstrate the viability of this technique for the new 600 MW boiler that was already partially built.

PILOT SCALE INVESTIGATIONS

Charbonnages de France decided to set up a research contract with the International Flame Research Foundation, Ijmuiden. A first trial series was carried out in April 1982 in order to verify that the GARDANNE coals had a specific behaviour with regards to SO_2 capture with sorbent injection and to quantify the extent of sulphur retention in the ash.

The experiments were carried out under the following conditions :

- 2.3 MW thermal input in the 6.25 m long, 2 m square IFRF n° 1 furnace,
- around 50 % heat extraction equivalent to flue gas temperature of 1000 °C.
- An IFRF circular burner with variable swirl and provision for staging of the combustion air with up to 50 % of the air being injected through four tertiary air ports.

The details of the experimental conditions and the results have been fully reported elsewhere (1) & (2) but it is worth recalling the main results :

- The parameter having the major influence on efficiency of SO_2 capture was found to be flame temperature. With a washed coal and $Ca(OH)_2$ injection the reduction of SO_2 emissions went from 52 % up to 80 % with a Ca/S of 2 when peak flame temperature was reduced from 1400°C to 1270°C. A similar effect was found with the high ash coal where natural retention of SO_2 in ash increased from 31 % to 40 % at a Ca/S of 2 when peak flame temperature was reduced from 1480°C to 1370°C.
- The reduction of excess air, particularly below 25 %, was found to have a strong negative effect on SO_2 capture for all sorbents.
- Staged combustion improved SO_2 capture only when it resulted in lower flame temperatures.
- Sorbent injection location did not have any significant effect on efficiency with these flames.
- $CaCO_3$ had very much the same efficiency when injected in the flame as when already present in the coal ("natural retention") : 40 % SO_2 removal at a Ca/S of 2 but $Ca(OH)_2$ gave much better results : more than 60 % removal under the same conditions.
- The use of an ultra-fine grinding for a carbonate (85 % smaller than 10 m) did not improve the results.

Based on these results the decision was made to carry out a second trial series under conditions that were different from several points of view :

- A 2.2 MW parallel flow burner was designed to simulate the near-field mixing pattern that takes place in the 50 MW unit of the power station. The combustion air distribution and velocity in the different ducts of the 2.2 MW burner were fixed at the same value as in the 12 MW burners of the boiler and the burners were geometrically similar (See Figure 2).
- Provision was made to simulate Flue Gas Recirculation in order to reduce flame temperature and assess the potential advantages (improved SO_2 reduction) and drawbacks (lower carbon burn-out) of such a technique. Combustion gases were produced by a separate natural gas fired combustor and had the following composition :

  . H_2O from 12 % to 17 %

  . CO_2 from 7 % to 10.5 %

  . CO from 0 % to 1.5 %

  . O_2 from 0 % to 7 %

These gases were cooled down to 200°C-300°C and could be injected in one or several air streams going to the burner. Under all conditions the total volume of flue gases coming out of the furnace was kept constant -the reference being 35 % excess air firing without F.G.R.- in order to simulate the conditions under which the boiler would have to be operated anyway. Thus when the level of F.G.R was increased up to 20 % of reference flue gas volume the actual excess air was reduced to about 15 %. Detailed results are available elsewhere (3) but it is worth looking through some salient results.

Figure 3 indicates very clearly that with the washed coal the injection of combustion gases in the combustion air reduces dramatically flame temperatures, particularly peak flame temperature which drops from 1400°C to 1240°C. This drop is in fact associated with a shift of the ignition front which moves downstream by more than one meter. The SO_2 capture that is achieved with $Ca(OH)_2$ mixed with the coal is very significantly improved by 20 % flue gas injection (SO_2 % in figure 3 is calculated relative to SO_2 emissions without sorbent injection). A further increase of the flue gas mass flow (25 %) did not improve the level of SO_2 capture.

Figure 4 presents results for natural retention of SO_2 when burning the high ash unwashed coal (Ca/S = 2). Here again it was found that injection of combustion gases reduced the peak flame temperature by more than 200°C by shifting the ignition front by about 1.5 m and resulted in an increase of SO_2 retention in the ash from 41 % up to 59 % (here SO_2 retention is calculated on the basis of potential SO_2 emissions with total conversion of fuel sulphur). However when furnace fouling became too high the same input conditions (i.e with 19.5 % F.G.R.) produced a flame having a temperature profile and SO_2 emissions similar to the baseline flame. In this case the higher furnace wall temperature (1020°C instead of 940°C) had a favourable effect upon ignition and the location of the flame temperature peak went upwards to the burner and was nearly as high as with the "pure air" flame.

It was clear that Flue Gas Recirculation could improve significantly SO_2 capture provided that it reduced peak flame temperature below 1250°C. This is illustrated by Figure 5 where the reduction of SO_2 emissions (on the basis of potential SO_2 emissions with total fuel sulphur conversion for better comparison) has been plotted as a function of peak flame temperature for washed and unwashed coal thus including ash and injected sorbent retention.

On the basis of these results it was decided to carry out a trial series on the 50 MWe boiler that would include experiments with Flue Gas Recycling.

EXPERIMENTS ON 50 MWe BOILER

The objectives of these experiments were first to verify on an industrial scale the encouraging results that had been obtained at pilot-scale and secondly to define the optimum combination of firing conditions, sorbent type and sorbent injection location that would give the highest sulphur capture on this unit in order to be able to design an injection system for the 600 MW unit.

General conditions of the trials

The boilers. Figure 6 shows a cross-section of the 50 MW unit. It is a tangentially fired boiler with four coal mills and four burner levels. Due to the characteristics of the GARDANNE coal (high ash, high calcium) the boiler had been oversized : the volume of the radiant section is about 50 % higher than it would be for a boiler fired with a more conventional bituminous coal. For the same reason the boiler is run with 35 % excess air in order to maintain a low temperature at the combustion chamber exit and avoid fouling.

The 600 MW unit was designed on the same basis. The cross-section of this unit presented in Figure 7 indicates that it has seven burner levels widely spaced, each burner level being fed by a vertical mill.

Operating conditions of the 50 MW unit during tests. For the tests, the operating conditions of the 50 MW unit were defined with the objective of simulating as closely as possible the normal operating conditions of the 600 MW unit particularly from the following points of view :

- residence time of solid particles in the combustion chamber,
- heat input in the burner zone area,
- flame and flue gas temperature.

These considerations led to the following conditions for the 50 MW unit :

- the load was fixed at 45 MW (electric output) with three levels of burners in operation. The upper level of burners was not in operation and was available for sorbent injection,
- burner axis was kept horizontal (zero tilt),
- excess air was kept at 35 % based on O_2 and CO_2 concentrations measured after economizer,
- combustion air distribution at burners as indicated in Figure 2.

Under these conditions the gas temperature at the exit of the radiant section was kept around 1100°C.

Measurements. Analyses of coal, particularly sulphur and calcium contents, were carried out regularly on coal samples which were taken systematically for every set of operating conditions.

Flue gas composition -O_2, SO_2, CO, CO_2 and NO_x concentrations- was measured at various points of the flue gas path in order to adjust inputs and to determine efficiency of SO_2 capture. In a few cases SO_2 concentration was measured at two points : after the economizer and after the electrostatic precipitator. This allowed verifying that no significant sulphur capture took place after the economizer and this sampling point was selected for all gas composition measurements.

At this point, gas temperature is between 400°C and 500°C and the gas sampling train was made of the following :

- a stainless steel sampling probe immediately followed by,
- a dust seperator (aerodynamic separation) followed by a porous membrane filter,
- a cooler regulated at 0°C for condensation of the moisture.

The dry and clean gas sample was then transported by a flexible PVC tube to a mobile laboratory for continuous analyses.

SO_2 concentration was measured with an Infra-Red Absorption analyser (LEYBOLD HERAUS, BINOS type). It was verified that no significant retention of measured species would take place in the whole sampling train. In particular there was no retention of SO_2 in the dry filter as long as it was kept dry. However the whole line was cleaned every half an hour.

Sorbents. Various sorbents were tested during the trials :

- An hydrated lime containing more than 98 % $Ca(OH)_2$ that was delivered in the form of a very fine powder (see Figure 8 for particle size distribution)
- A local limestone that was delivered in 0-12 mm grains and was pulverized in one of the coal mills (the one corresponding to the fourth level of burners) with a fineness that could be increased from 60 % smaller than 74 m to 90 % smaller than 74 m (Fig. 8). This limestone had a $CaCO_3$ content ranging from 92.2 % to 94.6 %.
- A Dolomitic "filler" containing 15.60 % $MgCO_3$ and 82.5 % $CaCO_3$ and that was delivered as a fine powder (see particle size on Figure 8).

Results of measurements without F.G.R

Natural retention. By firing coals having variable ash contents and therefore variable Ca/S ratio it was possible to determine the natural retention curve that is presented in Figure 9(a). A few points have been put on this curve but in fact the efficiency of sulphur capture by the coal ash was verified under many more circumstances and this curve can be used with confidence to predict the SO_2 natural retention of the GARDANNE coal from the value of Ca/S. The variation of the load did not significantly alter the efficiency of natural retention but the application of Over Fire Air had a slight negative effect upon SO_2 capture. It was observed that the natural retention was not significantly altered by boiler fouling (the furnace was cleaned by soot-blowers every five hours, before every new experiment).

Finally, it is worth pointing out that 40 % natural retention was achieved with a Ca/S of 2 which is similar to what was achieved in the pilot scale experiments (See Figure 4).

Sorbent injection. On Figure 9(b) are presented the results of $CaCO_3$ injection. The sorbent was pulverized in the available coal mill injected in the furnace through the transport air ducts of the fourth burner level. On this figure are presented the baseline natural retention curve, the natural retention values that were measured without $CaCO_3$ injection for various values of Ca/S (open symbols) and the increase in SO_2 capture that was achieved by injecting variable amounts of sorbent. The interesting thing is that $CaCO_3$ injection gave the same sulphur retention as natural retention and this was also found on pilot scale when $CaCO_3$ was injected with the circular swirl burner. This result is quite different than what has been observed by other workers with German brown coals (4) where it was found that calcium in the coal has an efficiency for sulphur capture which is always better than any sorbent. This specific behaviour of the GARDANNE coal is probably due to the presence of calcium in the form of large inclusions of $CaCO_3$ which are easily separated from the organic part of the coal during grinding and subsequently behave like separately injected $CaCO_3$ particles.

Some limited tests were carried out with the "dolomitic filler" and this product gave the same efficiency of SO_2 capture than the limestone.

It was also observed that the variation of $CaCO_3$ particle size within the range defined above (Figure 8) did not alter the results of SO_2 removal. This is in agreement with the pilot-scale trials which did not show any benefit in using an ultra-fine carbonate.

Figure 10 shows the results that were achieved by using the hydrated lime powder $Ca(OH)_2$. Figure 10(a) refers to the injection of the powder in the flame : $Ca(OH)_2$ was pneumatically transported up to the 12 operating burners and was injected on the burner axis or very close to it through simple pipes. Under these conditions the SO_2 reduction was not really better than with natural retention or $CaCO_3$ injection in the upper raw of burners. The same conclusion applies to Figure 10(b) relative to experiments where $Ca(OH)_2$ was introduced with the coal before the three operating coal mills.

The hydrated lime was also injected in the upper level of burners and this gave significantly higher SO_2 removal as can be seen in Figure 11. In a first series of experiments the sorbent was pneumatically transported from the storage bins and injected through the four corner burners of the upper level with a small quantity of air representing 1 % to 2 % of total stoïchiometric air requirement. The results which are presented on Figure 11(a) show that the SO_2 capture that was achieved with various combinations of ash content of the coal (i.e Ca/S ratio of the coal itself) and sorbent injection rate was always significantly higher than with previous experiments. Particularly it was possible to achieve more than 60 % SO_2 capture with a Ca/S ratio of 3 decomposed as follows :

- Ca/S = 2.4 for the coal giving around 45 % natural retention
- Ca/S = 0.6 with supplementary $Ca(OH)_2$ injection allowing to gain more than 15 % further retention

These results indicate that with $Ca(OH)_2$ there is definitely some benefit in injecting the sorbent above the high temperature zone of the furnace which was not the case with $CaCO_3$. A further improvement of these results could be obtained by blowing some secondary air in the fourth level of burners while injecting the hydrated lime as previously. This is indicated on Figure 11(b). It was indeed observed that when starting from a low ash coal (Ca/S ratio 1.5), the injection of increased amounts of $Ca(OH)_2$ through the upper burner level with small quantities of transport air had a strongly decreased efficiency when the amount of $Ca(OH)_2$ became too high (Ca/S equal 3). It was believed that mixing of the powder with the combustion gases was badly deteriorated at these high solid concentrations and the injection of secondary air (about 15 % of stoïchiometric air requirement) through the burner ducts around the sorbent injectors improved slightly but significantly the efficiency of sorbent utilisation.

Experiments with flue gas recirculation.

Prior to the experimental campaign provision had been made for re-injecting in the three levels of burners in operation combustion gases that were taken after the electrostatic precipitator. The system allowed injection of the flue gas in the transport air stream, in the adjacent air stream, in the secondary air stream or in any combination of these three possibilities. In all the tests involving F.G.R. the total volume of flue gas flowing through the boiler was kept constant by reducing excess air correlatively with the increase of F.G.R. mass flow.

Up to 20 % of flue gas volume was recycled but wherever the flue gas was injected no beneficial effect could be detected on SO_2 reduction levels neither by natural retention nor by sorbent injection.

Temperature measurements were carried out in various points of the furnace by inserting suction pyrometers as indicated by Figure 12. Many temperature profiles were taken without and with F.G.R. and although it is not possible to present them all the ones which are presented in Figure 12 are typical. The highest temperatures were recorded on the n°3 position, that is in the plane of the third level of burners and they were usually between 1400°C and 1450°C which is quite close to the peak flame temperatures recorded in the pilot scale experiments. However on the 50 MW boiler the mapping was not sufficiently detailed to be sure that these were peak flame temperatures. Flue gas temperature (n°1 position) were around 1100°C. The application of F.G.R. lowered the temperature profiles on position 3 by about 100°C (1300°C to 1350°C) but it did not alter the SO_2 capture results.

This is a major difference between the pilot scale experiments and the boiler experiments. One explanation can be put forward : in the pilot scale experiments it was seen that the reduction in peak flame temperature was due to a shift of the ignition front and was thus associated with a shift of the location of this peak downstream in the flame (See Figures 3 and 4). In the corner fired boiler this can work only to a point where one flame interferes with the one coming from the next corner. Therefore the latest ignition will be at the intersection of the flames. For the 50 MW boiler this represents a maximum distance of about 4 m. Considering that the burners in the boiler have a 12 MW capacity and assuming similarity of jet aerodynamics in the two systems these 4 m are equivalent to 1.7 m in the 2.2 MW flame. From Figure 4 it can be seen that to get a peak flame temperature lower that 1300°C -which is required for real improvement of SO_2 capture (Figure 5)- one needs this peak to be shifted by more than 1.7 m. It is worth pointing out that the assumption of a good similarity between the near burner aerodynamics of the two flames (2.2 MW and 12 MW) leads to predicting that the peak flame temperature measured with the 2.2 MW baseline flame -1440°C at 1.5 m- should be equivalent to a peak flame temperature of the same level at 3.5 m and that 1430°C was measured at 3 m from the burner mouth (location 3, 2 m from wall).

On the whole it is believed that the mechanism by which F.G.R. was effective, in shifting and reducing peak flame temperature in the pilot scale experiments with one burner in a coaxial furnace was not effective to the same extent in the corner fired 50 MW boiler and that peak flame temperature was not sufficiently reduced to really improve SO_2 capture.

Fouling and slagging

During the experiments which lasted over ten weeks there was no significant alteration of ash deposits on the heat transfer surfaces in the furnace nor in the convection banks. It should however be recalled that the PROVENCE POWER STATION BOILERS are oversized and superheater banks specially designed to avoid fouling.

CONCLUSION AND PROSPECTS

The experiments on the 50 MW boiler provided a set of reliable data on natural retention of SO_2 in the coal ash. They also demonstrated that Flue Gas Recirculation was not beneficial for SO_2 capture and the optimum injection location for $Ca(OH)_2$ has been found. These results made it possible to define the conditions of application of the direct sulphur capture technique to the 600 MW unit which was already under construction. On this unit the direct desulphurization will be applied as follows :

- Addition of limestone to the raw coal, before the mills in order to reach a Ca/S ratio of around 2.5 at the burners. At full load the mass flow of limestone will vary between 0 and 40 t/hr, depending upon the quality of the raw coal.
- Supplementary injection of hydrated lime ($Ca(OH)_2$ in order to reach 60 % sulphur capture (relative to potential SO_2 emissions). $Ca(OH)_2$ will be injected above the upper level of burners in operation with secondary air injection around the sorbent jets. At full load the mass flow rate of $Ca(OH)_2$ should be constant and around 15 t/hr to reach a total Ca/S ratio of 3.
- The experience gained with the 50 MW boiler has led to reconsider the design of the electrostatic precipitator : a fifth field has been added to the system initially designed with four fields.

Considering the costs of limestone -around 22 F/ton- and of hydrated lime -around 360 F/ton- and their respective efficiencies, the choice that was made was based on a compromise between to extreme solutions :

- The injection of limestone only, being much cheaper but resulting in a significantly higher solid loading in flue gas with associated drawbacks.
- The injection of $Ca(OH)_2$ only to minimize the solid loading in flue gas but with unacceptable costs.

With the assumption of 3500 hours of operation per year at full load, the operating costs of the sorbent injection have been evaluated at 0.015 F/kWh with an investment cost of 75 million F.

Under the same conditions the costs of an F.G.D. unit was evaluated at 0.05 F/kWh with an investment cost of 500 million F.

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Table 1

TYPICAL ANALYSES OF GARDANNE COALS
(as fired basis)

	Washed coal	Unwashed coal	
	Typical	Base coal	High ash coal
PROXIMATE, WT%			
Moisture	8.1	12.0	10.7
Volatile matter (including CO_2)	40.5	38.2	38.4
Fixed carbon	43.9	27.0	22.9
Ash	7.5	22.8	28.0
CO_2		9.1	13.2
ULTIMATE, WT% (including CO_2 from carbonate)			
Moisture	8.1	12.0	10.7
Ash	7.5	22.8	28.0
Carbon	63.0	45.7	41.4
Hydrogen	4.3	3.1	2.9
Organic sulphur	4.4	3.3	3.1
Pyritic sulphur	1.1	0.8	0.8
Nitrogen	1.6	0.9	1.2
Oxygen (DIFF)	10.0	11.4	11.9
HIGHER HEATING VALUE			
KCal/kg	6 290	4 360	3 790
Btu/lb	11 320	7 850	6 820
MJ/kg	26.335	18.254	15.868
ASH, WT%			
SiO_2	23.4	16.0	12.0
Al_2O_3	14.0	7.4	5.5
Fe_2O_3	13.4	5.0	5.4
CaO	22.3	51.0	59.9
MgO	2.7	1.5	1.3
Na_2O	0.3	0.2	0.15
K_2O	0.7	0.5	0.3
SO_3	22.6	16.0	13.6
Ca/S MOLAR RATIO	0.17	1.6	2.5
TOTAL SULPHUR CONTENT			
$Kg/10^6$ KCal	8.7	9.4	10.3
$lb/10^6$ Btu	4.8	5.2	5.7
g/MJ	2.08	2.245	2.46

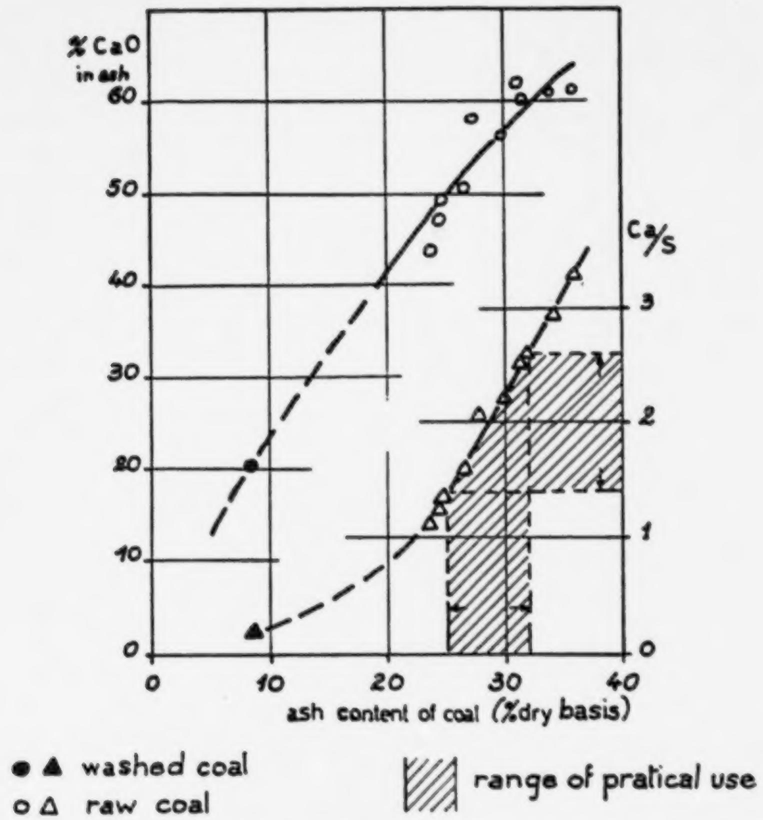


FIGURE 1 : CALCIUM CONTENT AND Ca/S MOLAR RATIO OF GARDANNE COAL

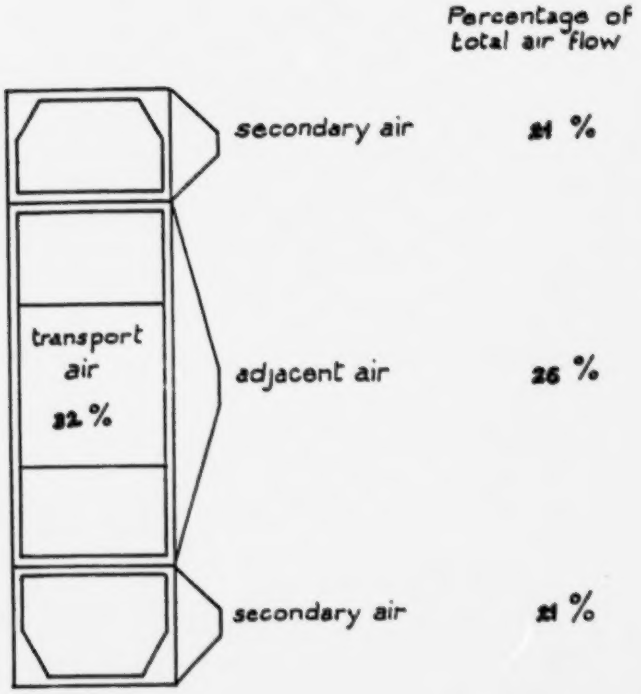
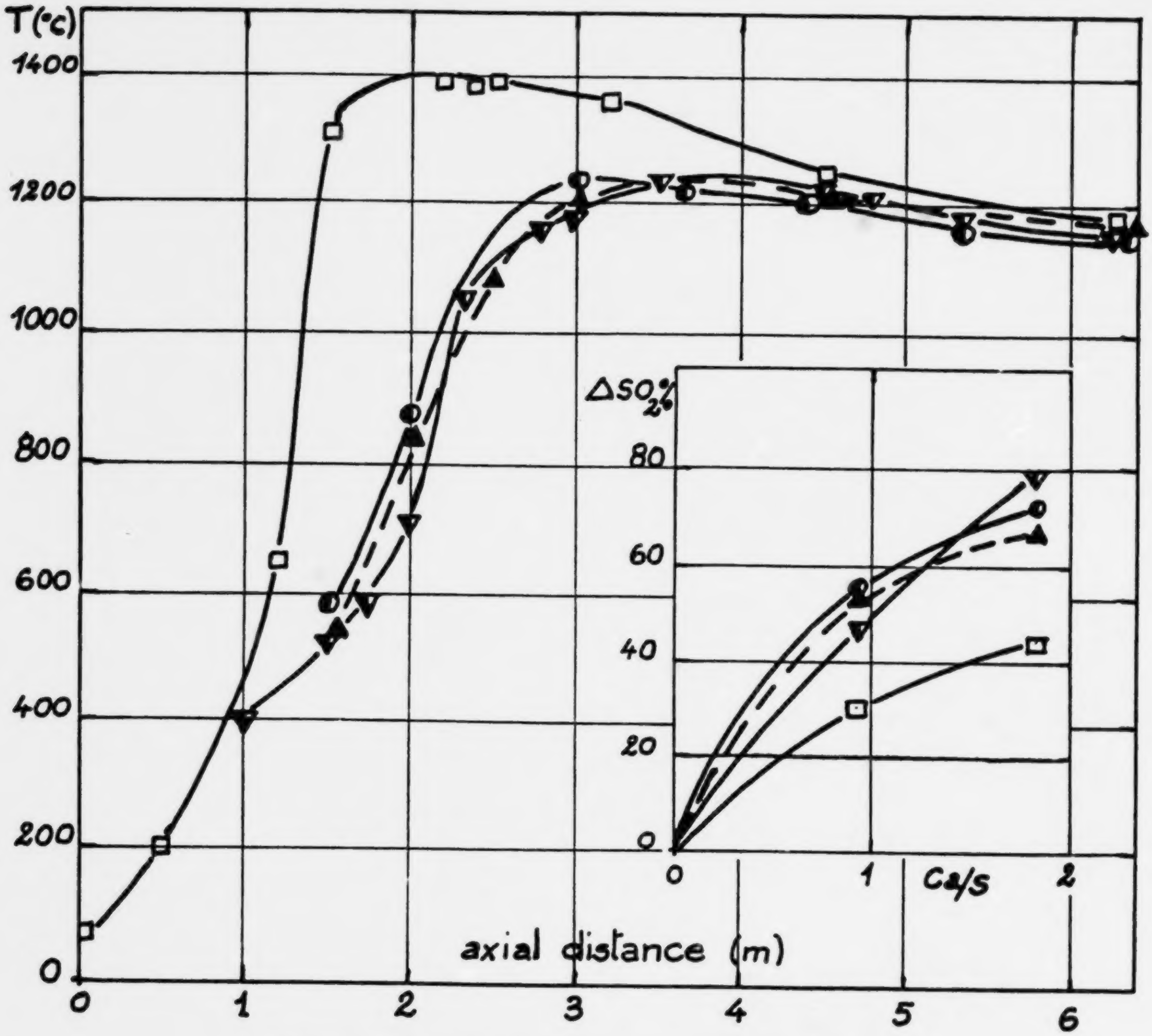
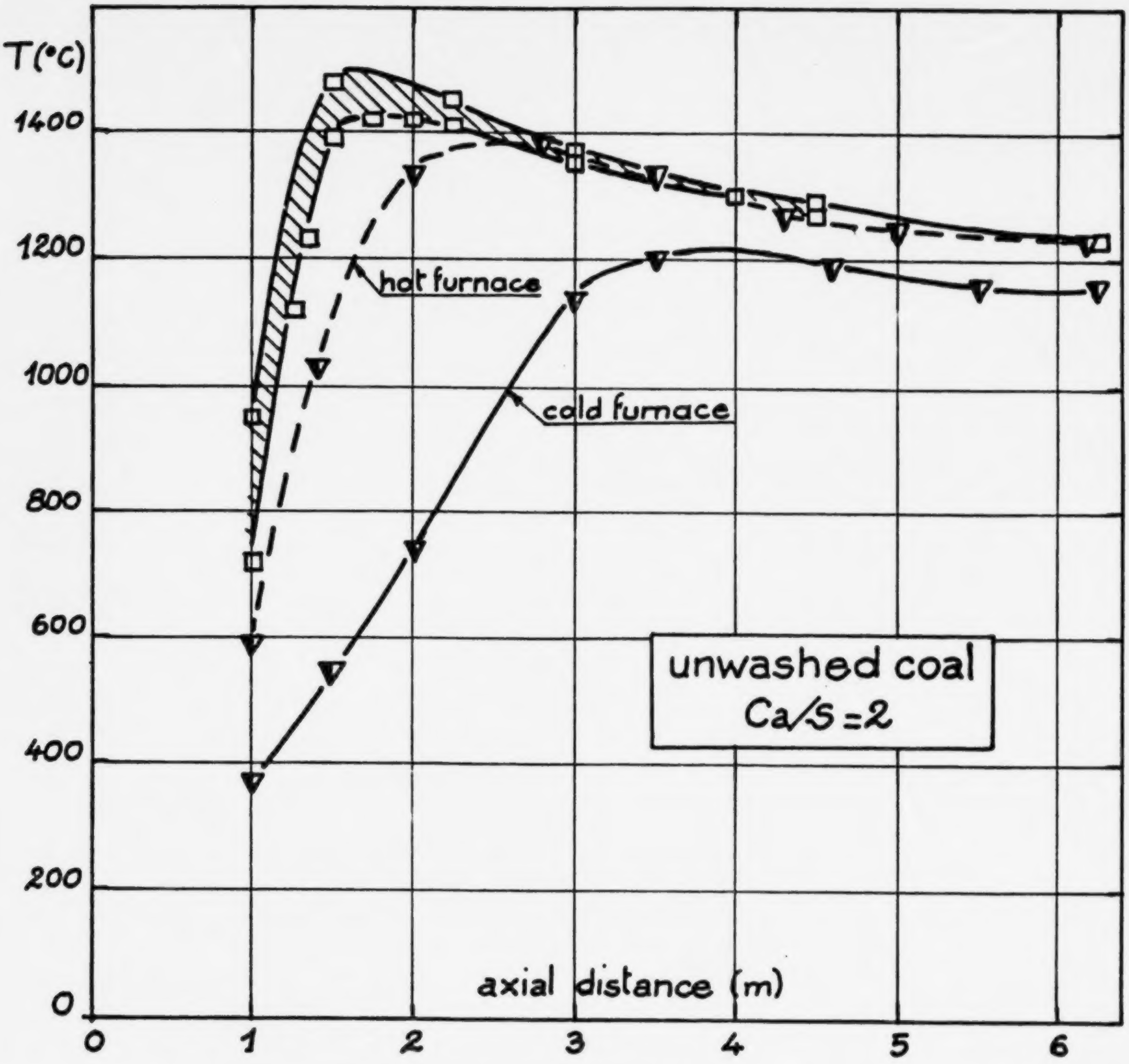

Percentage of total air flow
secondary air
21 %
transport air
32 %
adjacent air
26 %
secondary air
21 %

FIGURE 2 : PROVENCE POWER STATION N°1 UNIT (50 MW) - AIR DISTRIBUTION AT THE BURNERS



	Flue gas injection rate	Flue gas injection mode
□	0	—
▼	0.195	Adjacent and secondary air
◐	0.195	Adjacent and transport air
▲	0.245	

FIGURE 3 : WASHED COAL + $Ca(OH)_2$ MIXED WITH COAL ;
EFFECT OF FLUE GAS INJECTION ON FLAME TEMPERATURE
AND ON SO_2 REMOVAL RATES WITH A 2.2 MW BURNER



	flue gas injectionrate	flue gas injection mode	SO_2 in flue ppm dry	SO_2 capture %	NO_x ppm dry	O_2 % in flue
□——□	0	—	2545	41	1020	5.5
▽——▽	0.195	adjacent and secondary air	1900	59	480	2.0
▽- - -▽	0.195		2604	41	660	1.9

FIGURE 4 : UNWASHED COAL ; EFFECT OF FLUE GAS INJECTION AND FURNACE FOULING ON FLAME TEMPERATURE AND SO_2 NATURAL RETENTION WITH A 2.2 MW BURNER

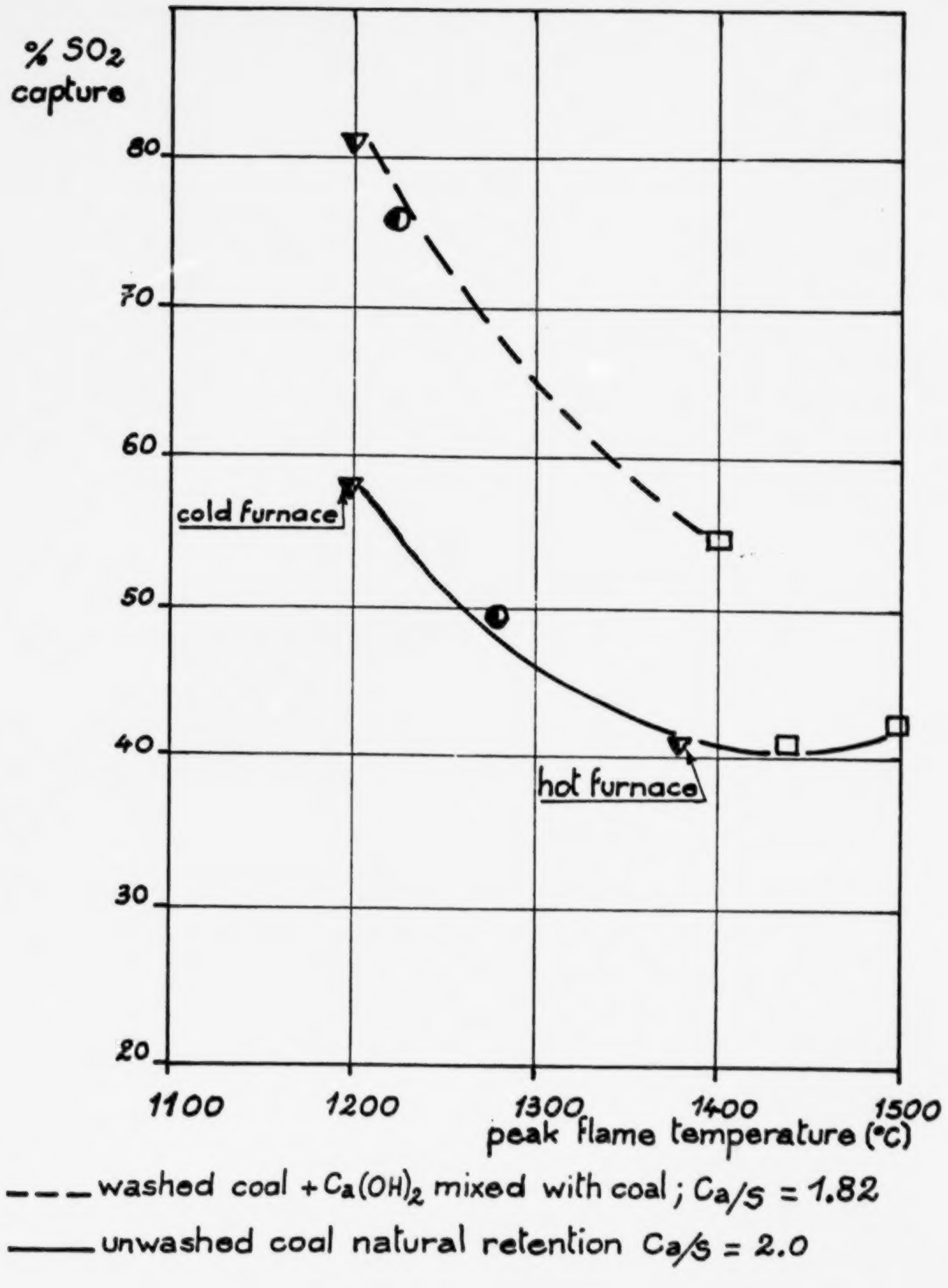


FIGURE 5 : EFFECT OF PEAK FLAME TEMPERATURE ON SO_2 CAPTURE WITH 2.2 MW BURNER

CENTRALE DE GARDANNE
Générateur de vapeur de 200-240 t/h

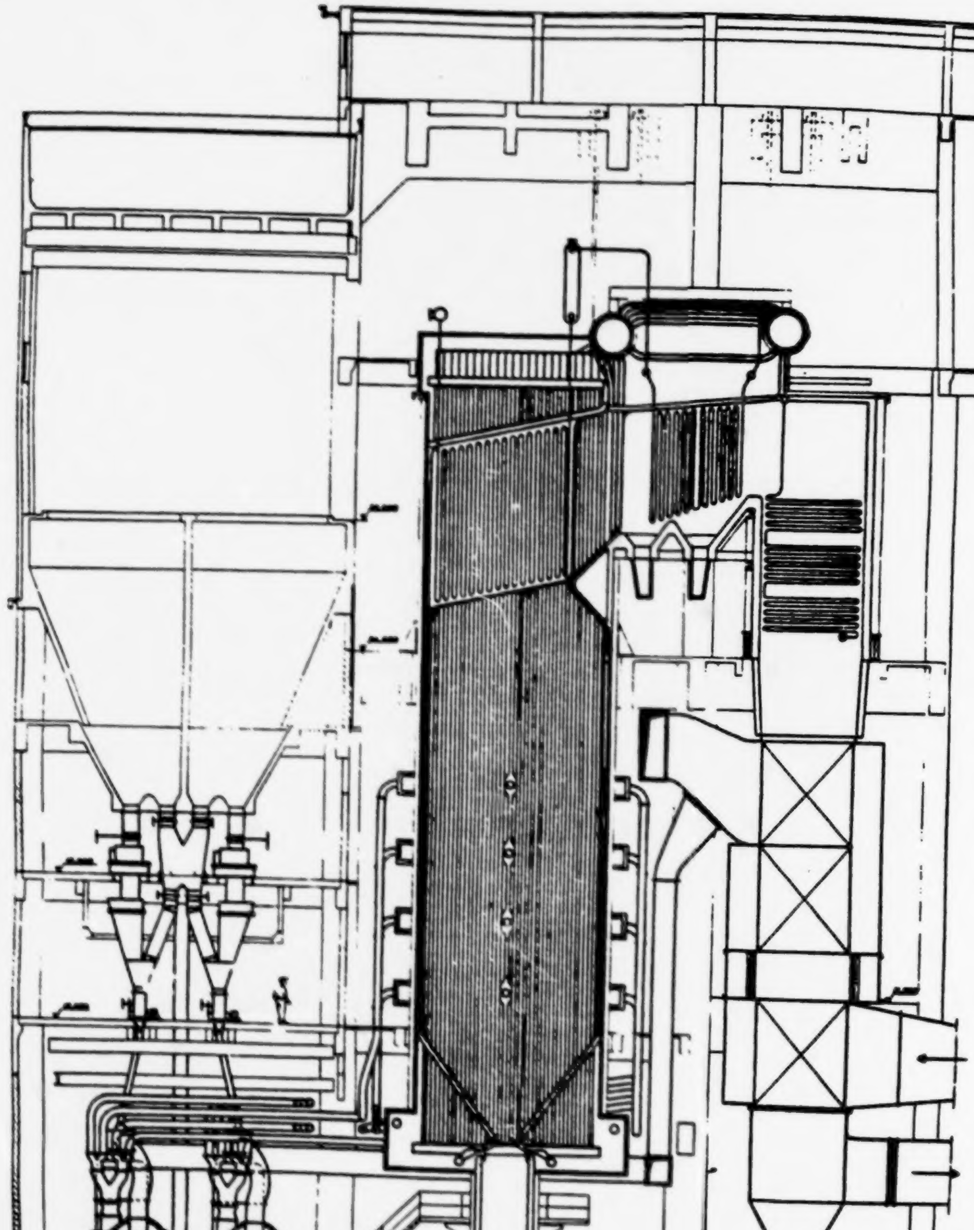


FIGURE 6 : 50 MW BOILER

HOUILLERES DE BASSIN DU CENTRE ET DU MIDI
CENTRALE DE PROVENCE - TRANCHE 5 - 600 MW
Generateur de vapeur

Vaporisation : 1787 t/h
Pression vapeur surchauffee : 181 bar
Temperature de surchauffe : 542 C
Temperature de resurchauffe : 541 C

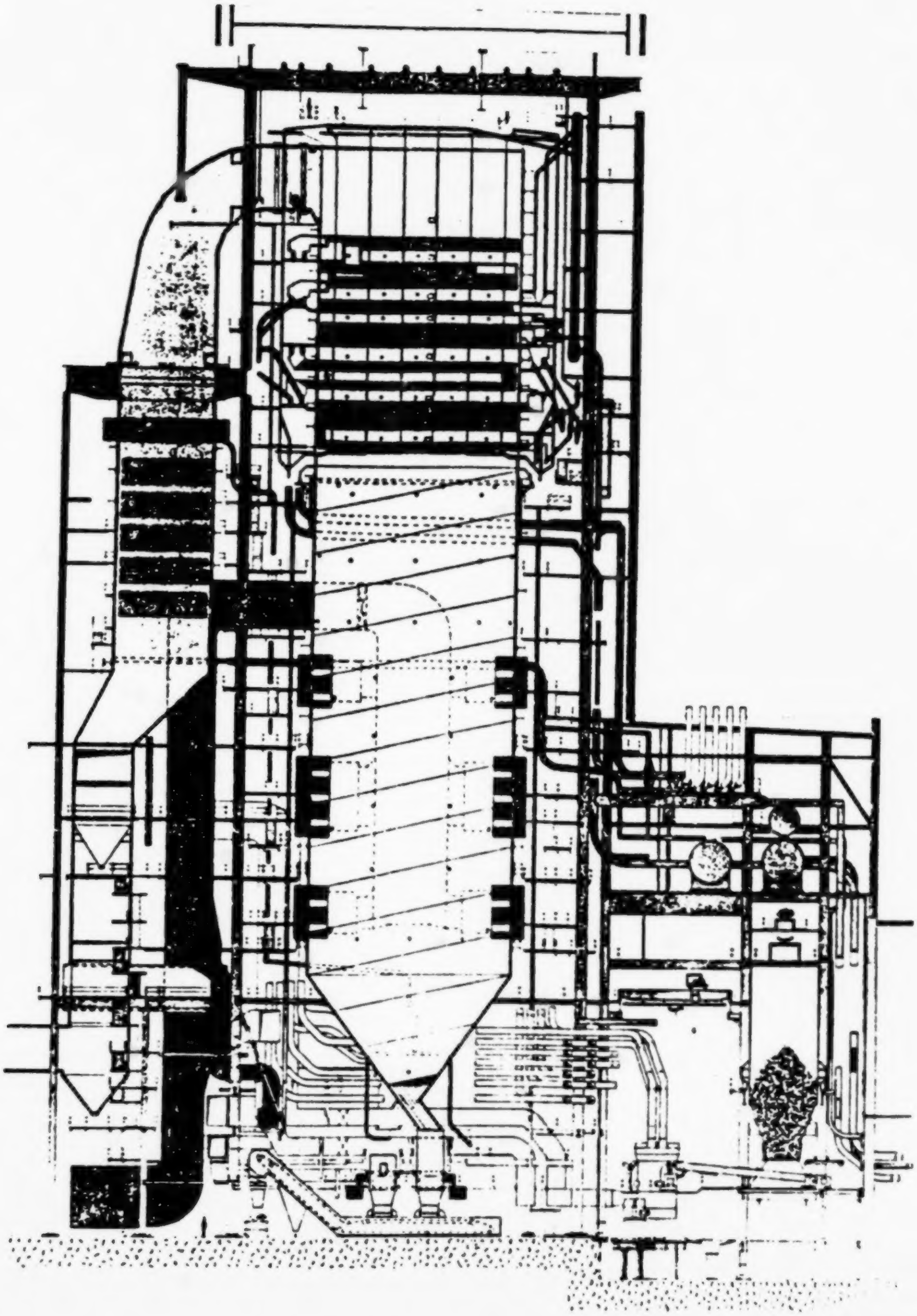


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FIGURE 7 : 600 MW BOILER

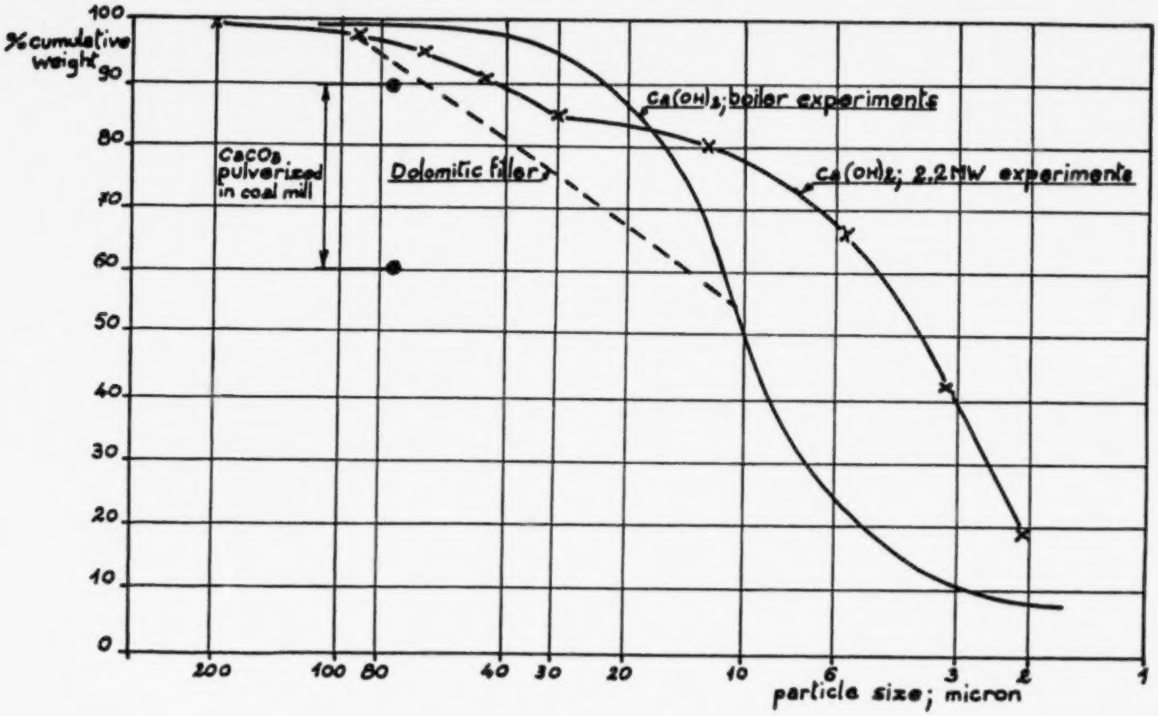
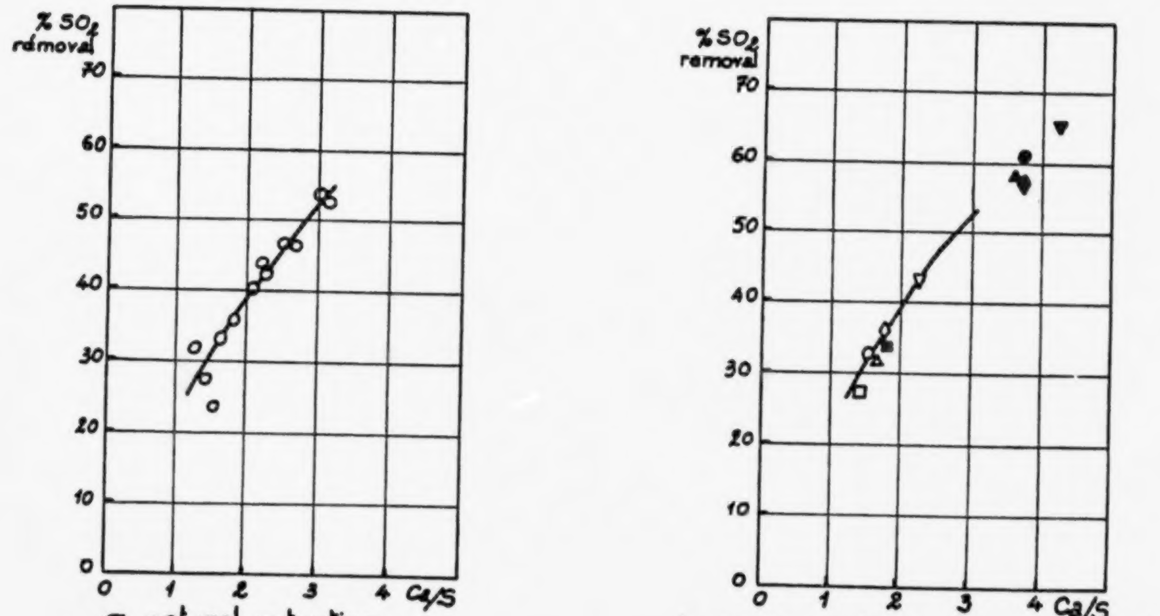


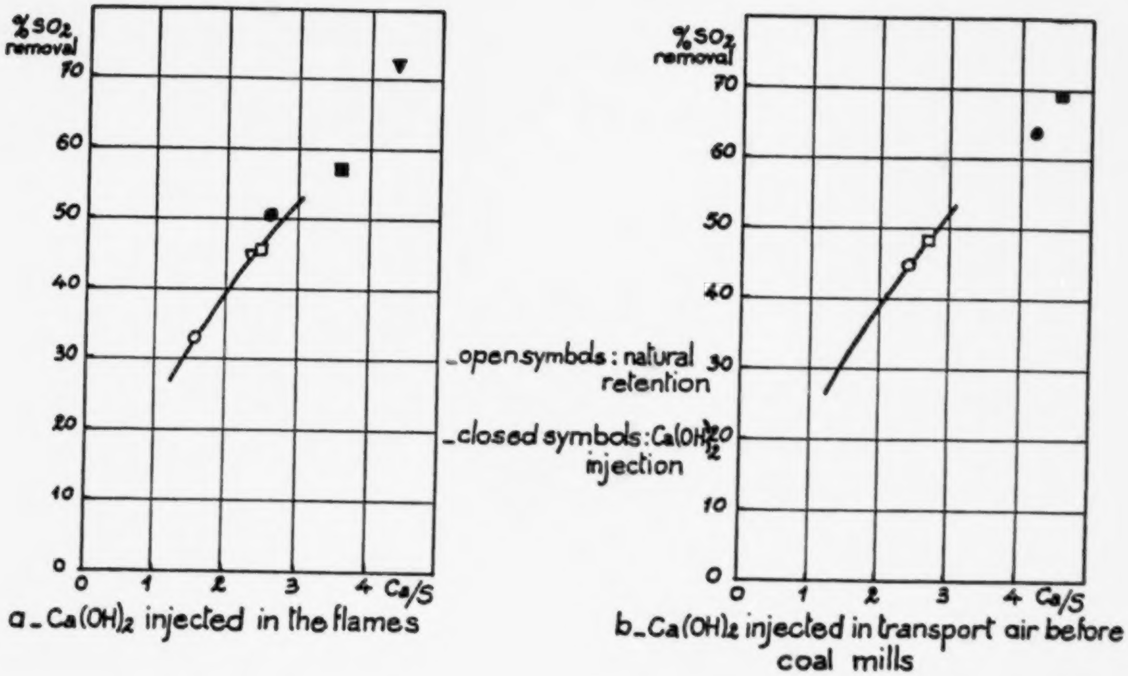
FIGURE 8 : PARTICLE SIZE DISTRIBUTION OF INJECTED SORBENTS



a - natural retention

b - CaCO₃ injection in upper burner level
- open symbols : natural retention
- closed symbols : CaCO₃ injection

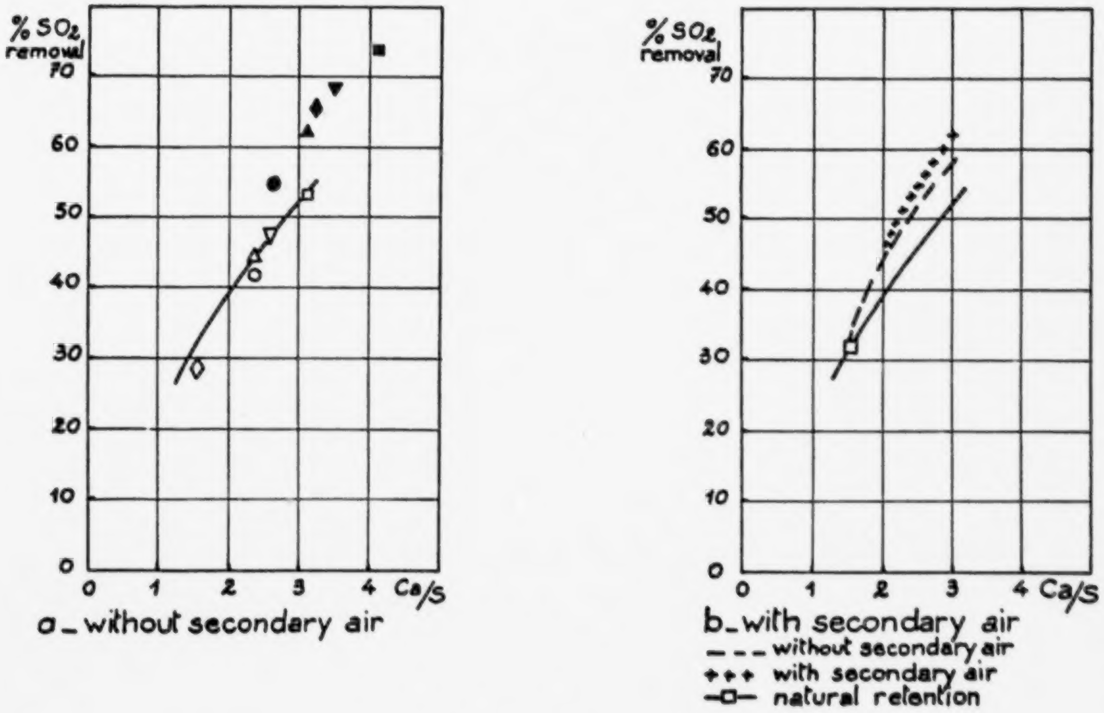
FIGURE 9 : 50 MW BOILER EXPERIMENTS



a _ Ca(OH)$_2$ injected in the flames

b _ Ca(OH)$_2$ injected in transport air before coal mills

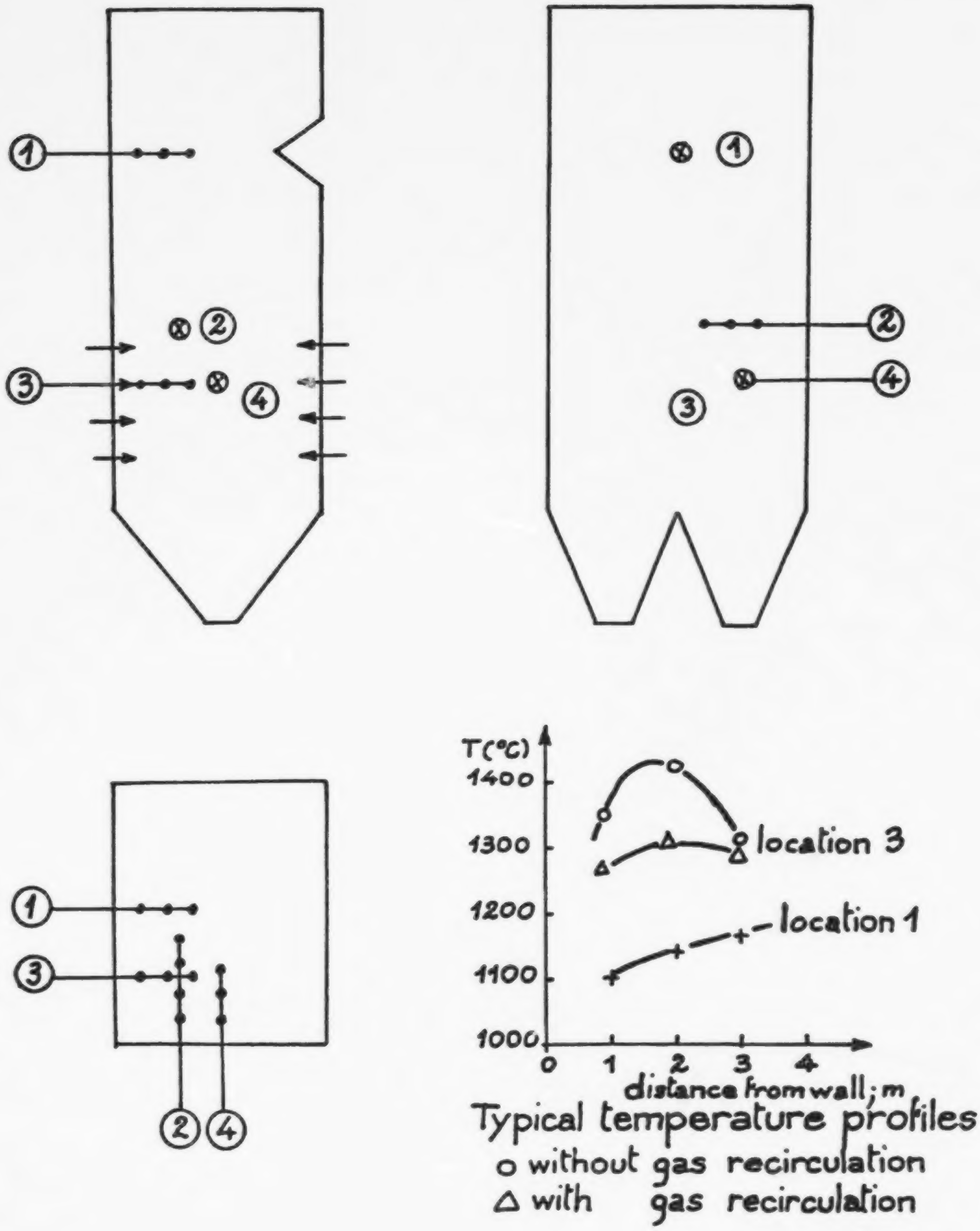
FIGURE 10 : 50 MW BOILER EXPERIMENTS ; Ca(OH)$_2$ INJECTION IN OPERATING BURNERS



a _ without secondary air

b _ with secondary air

FIGURE 11 : 50 MW BOILER EXPERIMENTS ; Ca(OH)$_2$ INJECTION IN THE UPPER BURNER LEVEL


①
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②
③
④
①
③
②
④
T(°C)
1400
1300
1200
1100
1000
0
1
2
3
4
distance from wall; m
location 3
location 1
Typical temperature profiles
o without gas recirculation
Δ with gas recirculation

FIGURE 12 : TEMPERATURE MEASUREMENTS IN 50 MW BOILER

DIRECT DESULFURIZATION AT THE 700-MW WEIHER III UNIT

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LABORATORY TESTS, FIELD TRIALS, AND APPLICATION OF FURNACE LIMESTONE INJECTION IN AUSTRIA

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ABSTRACT

In Austria six boilers ranging from 20 to 330 MWel having tangential firing or wall-firing are equipped with furnace injection. In all cases the limestone powder is introduced with the secondary air. Addition of the additive through the coal mills was less effective. Ca/S molar ratios of 3 to 4 gave average sulfur removal rates of 50 to 60 %, depending on the type and size of the furnace and on fuel. Fouling is a serious problem with hard coal at full load, but not at all at reduced load and only under certain circumstances with lignite.

Furnace conditions were simulated in laboratory experiments by putting single limestone particles with diameters from 3 to 100 µm for 3 to 20 seconds into a hot flue gas stream. The question on reaction rates as a function of particle size, SO_2 concentration, temperature (900 to 1150°C) and residence time could be answered.

Experiments in a pilot bag filter with 1 m^2 filter area and jet cleaning showed that the poor utilization of dry limestone in furnace injection of only 10 % can be improved to up to 26 % if the ash is separated from the flue gas, optionally milled, treated with steam and reinjected into the cold flue gas. Sulfur removal of up to 80 % and SO_2 outlet concentrations as low as 100 ppm were achieved.

LABORATORY TESTS, FIELD TRIALS, AND APPLICATION OF FURNACE LIMESTONE INJECTION IN AUSTRIA

With "FURNACE INJECTION" in general the supply of some additive in addition to the fuel into the combustion chamber of a boiler is meant. The function of the additive is to absorb or react with some gaseous or solid component, which should not be emitted to the environment mostly in order to prevent the environment from damage. "Acid" gases like SO_2, SO_3, HCl, HF (and in principle CO_2) can react with basic solids like CaO, MgO, Na_2O and so on. Since the Austrian mountains are built of limestone rock to a great extent, limestone should be the basic agent and since Austrian brown coals hardly contain any fluorine or chlorine only the sorption of SO_2 and SO_3 by $CaCO_3$ shall be considered. The basic reactions are:

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad (1)$$

$$CaO + SO_2 + 1/2\ O_2 \rightleftharpoons CaSO_4 \qquad (2)$$

$CaSO_4$, unreacted $CaCO_3$ and CaO are the only products. Other compounds like CaS or $CaSO_3$ were only produced in laboratory scale work, but were never found in the ashes of commercial, coal fired installations, probably because the flue gas always contains more than 4 % of oxygen.

Magnesia seems not to form stable sulfur compounds at furnace conditions, but it may help to improve the utilization of the calcium in a dolomitic additive.

Since the equilibrium of equation (2) is temperature sensitive the temperature of the furnace as a whole and the method of addition is of major importance for the process.

The additive may be supplied to the furnace by different methods:

- addition to the coal before it enters the mill
- injection into the mill
- injection into the furnace at a selected position
- injection into the furnace with the overfire or underfire air (secondary or tertiary air with wall burners).

Based on the results from large scale trials by Österreichische Draukraftwerke AG (ÖDK) in Austria furnace limestone injection has become a common practice. All suitable boilers are equipped with injection facilities and achieve more than 50 % sulfur removal. The large scale applications are backed up by laboratory experiments. Pilot scale trials showed, that a considerable improvement of the poor additive utilization is possible if the ash is treated and collected on a fabric filter.

Experiments

Most of the experiments were done on three different plants of ÖDK, i.e. Voitsberg No.2, St.Andrä No.2 and Voitsberg No.3, which are listed with other plants having LIMB in Table 1. All three plants have beater mills with hot gas recycle from the combustion chamber and corner firing. The fuel is a local brown coal with high ash and water content. The sulfur content changes in a wide range from 0,4 to 1,5 %. The SO_2-concentration in the flue gas may change over a factor two within twenty minutes; for very short times peaks up to 7000 mg/m^3 may occur.

Additives. The additives came from different quarries within Austria, having different chemical compositions. As can be seen from Table 2, some of them were very pure calcites, some were dolomitic. Also the particle size and particle size distribution was very different for the test-powders, as can be seen from Figure 1.

Furnace Temperature. It was known from literature (1, 2, 3, 4, 5) that the furnace temperature greatly influences the efficiency of the process. Therefore before any changes were made on the system or the mode of operation the temperature distribution throughout the combustion chamber was measured with a bare thermocouple (6). By doing so not the true flue gas temperature was determined, but the temperature, which a lime particle at this particular position in the furnace might obtain. The thermocouple was positioned at the hottest point in the furnace and the temperature recorded throughout all testruns, although the location of the hottest point may move when the operating conditions are changed e.g. through flue gas recycle or increase of the air factor.

Already the first testruns showed, that in many applications a reduction of the furnace temperature below normal operating conditions will be required, in order to achieve a satisfactory limestone utilization. Methods to reduce the furnace temperature are: cold flue gas recirculation, increase of air factor and reduction of boiler load. The injection of water in addition to the moisture of the coal was not investigated.

The hottest furnace temperatures were

Voitsberg No.2	1150°C
St.Andrä No.2	1227°C
Voitsberg No.3	not measured.

The relation between furnace temperature and additive utilization is treated in an earlier publication (7). In short: If 17 to 18 % of the flue gas flow is recycled, limestone utilization and desulfurization efficiency may increase by a factor 1.3.

If the furnace temperature becomes as low as 950°C (which is only of academic interest in pulverized fuel combustion) the limestone utilization drops again because of incomplete decomposition of the limestone.

It seems, that the optimum furnace temperature for the best additive utilization in a commercialsize boiler is close to 1070°C. Whether this is obtained through a very moist fuel, operational measures or an appropriate design of the combustion chamber should not matter.

Mode of Limestone Addition. Limestone powder was supplied by truck and stored in silos, from where it was dosed by star valves onto a conveyor belt and dropped on the coal or into a pneumatic feed line.

If the limestone powder is dropped onto the conveyor belt the dust developing at the dropping points at the end of the belt causes quite some annoyance.

All later experiments and all permanent installations apply pneumatic conveying which does not cause any problems - if it is properly designed. In one experiment the limestone powder was injected into the coal mill, but desulfurization was less than with other methods. Today all installations inject the additive in the overfire air duct, since this causes no operational problems and gives the highest desulfurization and best limestone utilization.

Electrostatic Precipitator. All plants are equipped with electrostatic precipitators of appropriate size, such that dust concentrations of 150 mg/m^3 and lower are usual operating conditions. Only the ESP of St.Andrä No.2 will not fulfill future emission standards and will be replaced by a baghouse.

During the experiments with limestone addition the dust concentration in the clean gas was measured and compared with measurements done shortly before and after the trials. A significant difference in the emission could only be found with the ESP of St.Andrä No.2 and with unpractically high additive/fuel ratios, e.g. 170 kg of additive per 1000 kg of fuel (which equals a Ca/S ratio of about 7).

Results. A set of results, obtained in Voitsberg No.2 with the limestone powders listed in Table 2, of which the particle size distributions are given in Figure 1 are given in Table 3. In this set of experiments the additive was blown into the hot gas suction duct leading from the upper part of the combustion chamber to the coal mill. Today we know that this method of addition gives least desulfurization and additive utilization. However this set of experiments compares many powders and operation with and without flue gas recycle.

The desulfurization D(A) was calculated from the formula

$$D(A) = \frac{\text{Sulfur in ash}}{\text{Sulfur in coal}}$$

which showed the most reliable results. In Figure 2 the results of Table 3 are plotted against the powder/sulfur ratio. This powder/sulfur ratio gives a better indication of the effectiveness of a particular powder than the Ca/S ratio (which is often used), especially if calcitic powders are to be compared with powders which contain magnesia or inert substances.

Further in Table 3 the sulfurdioxide concentration in the flue gas duct and the molar ratio of (Ca + Mg)/S entering the system is shown. All values are determined from the ash analysis. This means that the calcium and magnesium which are contained in the coal ash are also included. This is justified, since we found that the utilization of the earth alkaline metals contained in the ash is about equal to the utilization of the additive. Although magnesia is supposed to form no compounds with sulfur oxides under the prevailing conditions the sum of the moles of earth alkaline metals was calculated, since magnesia seems to promote desulfurization. ALKU is the molar ratio of (Ca + Mg)/S found in the ash.

In all experiments the ashes from the furnace bottom and the filter ash were sampled, analysed and the results summed up in accordance with the relative mass fractions of the ash flows.

In Table 3 and Figure 2 run numbers 2, 3 and 5 had no flue gas recycle, all others had. Since flue gas recycle (at least at Voitsberg No.2) increases the desulfurization by a factor 1.3, the desulfurization of these runs as it would have been if they had flue gas recycle can be estimated and plotted into Figure 2. With these three points corrected to equal operating conditions a relative ranking of the different powders becomes possible, although the sulfur dioxide concentration, mainly due to the changing coal properties, but also due to reduced additive dosing, was not constant. The ranking of the powders is: D, F, E, B, C, A, G, H and I. The small difference between powders B, E, F and D may be due to experimental inaccuracy.

Furnace limestone injection may cause three different kinds of losses:

- heat of decomposition of the limestone
- increased loss of carbon in the ash
- increased stack loss through higher stack temperature.

The heat required for decomposition of the limestone as well as the heat gained from the formation of calcium sulfate can easily be calculated. Together with the heat required for heating up the additive to the flue gas temperature the heat requirement of the additive may amount up to 1,5 % of the heating value of the fuel.

Increased loss of carbon in the ash may occur when the additive is added to the coal. No increased loss of carbon could be found if the additive was injected with the overfire air.

If the temperature of the combustion chamber was reduced by recycling cold flue gas or increasing the air factor the stack loss increased because of a higher gas temperature - and in the case of the greater air factor - an increased gas mass flow to the stack.

Injection of the additive with the overfire air gives much better desulfurization and additive utilization than any other method of addition. This can be shown by comparing runs which both used additive G but one time added to the coal on the conveyor belt, and the other time injected with the overfire air.

This experiment was done in St.Andrä No.2. The runs with comparable operating conditions are listed in Table 4. The St.Andrä No.2 plant is - because of its high furnace temperature - not well suited for LIMB which can be seen from the poor utilization of the earth alkaline metals (ALKU) of run numbers 2 to 7. If the limestone powder is injected with the overfire air ALKU increases by a factor 1.7. About the same improvement was found in Voitsberg No.2 after retrofitting the plant with permanent injection equipment.

Application of Furnace Limestone Injection

Operating Plants with LIMB. At present four installations with 6 boilers operate with LIMB (Table 1). The normal dosing rate is 80 kg of additive per 1000 kg of brown coal.

All boilers inject the additive with the overfire air respectively the secondary air if wall firing is applied since this method gave the best additive utilization and no operational problems.

Experience with Operating LIMB. Desulfurization in all cases is better than 50 %. With the smaller plants it may be better than 60 %. In Figure 3 the desulfurization obtained in Voitsberg No.3 during the first full operating period is plotted. The full line shows the desulfurization averaged over a period of one week. The dotted line shows the average per month with the days on which operational problems did not allow normal operation disregarded (which is in compliance with Austrian legal regulations). During this period the Ca/S ratio was 2.5 if a dolomitic powder was used and 4 with calcite.

Deposition of slag or ash is never a problem. Only Voitsberg No.3 has soot blowers, which are operated once a day. In the other plants probably some more build ups of deposits in the convection section were observed which were removed during the annual outage. The build-ups had no strength and were removed easier than the normal deposits of earlier years. The heat transfer in the convection section was not changed by the deposits.

The ash contains up to 20 % of Calcium in the form of CaO which reacts with the water after wetting of the ash. This may lead to the development of water vapor if the ash is hot before wetting. Cold ash - e.g. after pneumatic conveying over a few hundered meters distance - reacts slowly with the water and thus develops no steam. The water flow into the ash wetting equipment (mixer) must be accurately controlled, otherwise the mixer may plug up with solidified ash.

Future of LIMB in Austria

Two different developments can be foreseen for the near future, depending on whether the particular plant is expected to have a long or a short remaining life time.

Old Plants. All old plants - like Voitsberg No.2 - are of smaller size and will comply with the legal requirements, at least with what they are now, if they burn the local brown coal and apply LIMB.

New Plants. Several new power plants are being built at the moment but only Voitsberg No.3 is fired with brown coal and equipped with LIMB. The other plants will be equipped with conventional FGD. Voitsberg No.3 too gets a wet FGD which treats 100 % of the flue gasflow, but it will be difficult to comply with the emission standard of 400 mg/m³ if a high sulfur peak of 7000 mg/m³ occurs. To achieve the required high degree of desulfurization a combination of LIMB and wet FGD will be applied in Voitsberg No.3 according to Figure 4. Under normal operating conditions the LIMB equipment will be stand-by and no limestone will be injected. If however a SO_2 concentration higher than about 4000 mg/m³ is measured in the raw gas the LIMB will be activated within a few seconds in order to remove some of the sulfur dioxide from the raw gas. By this "peak shaving" a more stable operation of the wet FGD is achieved as is illustrated by Figure 5 (8).

LABORATORY EXPERIMENTS ON LIMB

The SO_2-pickup of limestone and dolomites was investigated by several researchers (9, 10, 11, 12, 13). The investigations however did not cover the ranges of residence times, temperatures or grain sizes which are practical in LIMB. Consequently it was our task to investigate the SO_2-pickup of powders with particle diameters of 60 µm or smaller, at temperatures as high as 1100°C and exposure times of three to twenty seconds in a flue gas atmosphere with 1000 to 2000 ppm of SO_2.

Experimental Setup

Synthetic flue gas could be produced from an experimental furnace which burned natural gas with a varying air excess and with different amounts of SO_2 added to the air before combustion. The flue gas temperature could be adjusted by the burner throughput. Since the heat loss remains almost constant, a smaller throughput gives a lower flue gas temperature.

The 200 mg powder sample was distributed evenly on a 500 mm diameter felt of heat resistant material (Al_2O_3 fibers) and covered with an other layer of felt. A thermocouple from 0,1 mm thick wires was also imbedded between the two felt layers. This raw sample was inserted into a "pipe", as shown in Figure 6. Gas was sucked through the pipe by a vacuum pump, and the gas flow measured. The pipe could easily be moved into and out of the flue gas stream which left the furnace (Figure 7). The actual temperature and residence time could be read from the recording of the thermocouple.

Each sample was analysed for Ca, Mg and S.

First Results

First results are shown graphically in Figures 8 to 11. Figure 8 shows the conversion of a calcite and a dolomite powder of a narrow size range between 25 and 28 µm as a function of time at different temperatures as the parameter. In this set of runs the SO_2 concentration could not be adjusted accurately due to technical reasons. Thus the SO_2 concentration is not the same in all runs! However, with the temperature of 950 to 960°C the best conversion could be obtained, although the SO_2 concentration was lowest. For the very short residence times of two and three seconds the higher temperatures gave a better conversion. This fact will be analysed more quantitatively in the future. The calcite seems to need more time for burning than the dolomite. But, if the residence time is long enough the calcite A picks up more SO_2 than the dolomite G. In all cases the conversion is defined by the formula:

$$\text{Conversion ALKU} = \frac{\text{moles of S in sample}}{\text{moles of (Ca + Mg) in sample}} \qquad (3)$$

The effect of temperature on the conversion of different powders is shown in Figure 9. Again the experimental conditions are not perfectly the same. Nevertheless clear trends can already be deduced: The dolomite powder G gives a very high conversion of (Ca + Mg) at 950°C and drops off markedly at higher temperature. The calcite powder A seems to be less sensitive to temperature.

Surprisingly low conversions were obtained with powders J and K, although these had by far the smallest particle diameter. The only possible interpretation is, that powder J comes from a chemical precipitation and therefore may consist of very perfect cristals which do not produce a great reactive surface. Powder K is a milled, very white marbel. It takes at identical conditions some what more sulfurdioxide than powder J but is significantly less active than the more "ordinary" powders, despite the smaller particle size.

The effect of particle size, shown in Figure 10, is not dramatic, as long as the particle diameter is somewhere between 25 und 120 µm. Two runs with a very fine fraction of dolomite G showed a surprisingly high conversion of 50 %, which means, that 85% of the calcium had been converted.

The effect of SO_2 concentration on conversion is shown in Figure 11. Since the shape of this curve is very similar to the ones of Figure 8 - for comparison: doubling the residence time from 10 to 20 seconds effects the conversion in the same amount as doubling the SO_2 concentration from 1500 to 3000 ppm - some common controlling mechanisms can be assumed, probably the build up of a restriction for diffusion of SO_2 to the CaO or simply the consumption of open pore volume.

Future Work

Future work will concentrate on

1 gather more information at residence times shorter than 5 seconds, temperatures around 1100°C and SO_2 concentrations at and below 1000 ppm. Also particles with 10 µm diameter of both, calcite and dolomite powders will be investigated.

2 Construction of a continous vertical flow reactor for residence times smaller than 5 seconds in order to produce larger samples of sulfated limestone for the determination of BET-surface,pore diameter and pore volume.

3 Try to identify the change of crystal structure during the first seconds of heating the particle with the aid of an electron microscope and x-ray diffraction.

SECONDARY UTILIZATION OF LIMB-ASH

Since the conversion of an additive injected into a pulverized fuel fired furnace in practice hardly exceeds 12 %, an other means must be found to utilize the CaO, which is contained in the ash with a three to eightfold excess relative to the remaining SO_2 in the flue gas. This high alkaline ash can be slaked and used as an absorbent in a spray dryer or in a wet FGD. Both applications may be economically advantageous under certain circumstances.

A more attractive method would be to increase the residence time of the additive particle in the flue gas and let it react with the SO_2. This can easily be achieved with a fabric filter. However the rate of reaction at usual operating temperatures is very small and as a result of this unpractically long residence times would be required. Only activation of the ash by some means can make the fabric filter work as a piece of desulfurization equipment.

From literature (14) it is known, that the sulfation of calciumoxide is a very slow reaction if the temperature is lower than 400°C. Reasonable reaction velocities are to be expected if calciumhydroxide is used as absorbent even at temperatures between 100 and 200°C. A number of dry processes are based on this reaction.

The missing step is the conversion of the CaO contained in the fly ash into an active form of $Ca(OH)_2$.

Activation of LIMB-Fly Ash

According to Schlegel (15) the CaO should react quickly with the up to 15 % H_2O of the flue gas. A number of trials with filters showed that this does not occur. Cutler (16) reported, that treatment of CaO with CO_2 at a temperature between 340 and 882°C did slow down a following hydration considerably. The fly ash was in contact with the CO_2 of the flue gas during cooling down. With the surface covered with $CaCO_3$ a following hydration will be slow.

But even if hydration of the CaO at an active site would occur, the SO_2 and CO_2 would react with the just forming $Ca(OH)_2$ immediately and build up an impermeable layer of $CaSO_3$ or $CaCO_3$ on all active surfaces. This coincidence of the hydration reaction with the sulfation/carbonation reactions could be the cause for the low sulfur capture of LIMB-fly ash in fabric filters.

Thus: The hydration of the CaO must occur in the absence of SO_2 and CO_2. This means: The ash must be separated from the flue gas, treated with steam and remixed with the flue gas for SO_2 absorption. An additional disintegration step before the steam treatment may speed up the hydration reaction and improve the absorption capacity of the ash.

The LIMB-FILTER Process

Figure 12 shows a process, which realizes the required steps

- separation of the ash from the flue gas
- mechanical disintegration
- steam treatment
- recycling of the treated ash into the flue gas stream and deposition, preferably on a fabric filter.

A process of this kind can be very attractive to those boiler operators, who have to retrofit their plant with new dust removal equipment because of new, more stringent regulations.

Experiments

To show that the LIMB-filter works, a pilot jet filter having one bag with 1 m^2 filter area was operated at the cogeneration plant at Graz (FHKW of Table 1) during LIMB trials with ash produced in these trials. A diagram of the plant is given in Figure 13.

For the tests clean flue gas was taken downstream of the ID-fan of boiler No.3, flow, temperature and SO_2 concentration were measured. This flue gas flow contained less than 150 mg/m^3 of dust. The flue gas passed through the single filter bag, temperature and SO_2 concentration were measured at the exit. The bottom of the filter casing could hold up to 14 kg of ash, which was fluidized with steam. The central nozzle formed a spout, which mixed partially with the incoming flue gas. By doing so a redistribution of the ash in the flue gas stream was achieved. The ash could be lock hoppered in and out during the experiment. Actual operation however was batchwise and the lock hoppers were only used for sampling. The exposure time for one batch of ash was between 6 and 41 hours.

The SO_2 concentration of the raw gas changed during one run between 330 and 830 ppm. The SO_2 concentration in the exit gas was sometimes brought down to 100 ppm.

Results

Desulfurization. The experiments were done in the months April and May when the boiler load of the cogeneration plant had to be turned down to only 50 % of its normal rating. As a result, the flue gas conditions too changed in a wide range. Since it was not possible to measure the SO_2 concentration before and after the filter at the same time, it is no surprise, that the calculated degree of desulfurization scatters in a wide range. Figure 14 shows measured degrees of desulfurization as it is obtained with one batch of ash in the filter alone. Thus the desulfurization in the furnace has to be added according to the formula

$$D_{\text{LIMB + Filter}} = D_{\text{LIMB}} + (1 - D_{\text{LIMB}}) \cdot D_{\text{in Filter}}$$

$$\text{with} \qquad D = \frac{\text{Sulfur}_{\text{in}} - \text{Sulfur}_{\text{out}}}{\text{Sulfur}_{\text{in}}} \qquad \text{Degree of Desulfurization}$$

The most reliable basis to calculate the pickup of sulfur is the ash analysis like in LIMB-experiments. The analyses for five runs are given in Table 5. The first five rows show the composition of the ashes after utilization in the pilot filter. The most important figure is the calcium utilization which is 0,26 in run No.7 and higher than 0,2 in three more runs. The sixth column shows a typical composition of the LIMB-ash before it was charged to the pilot plant.

When using air instead of steam in the primary nozzle (to generate the spout) the calcium utilization is considerably less, although the other operating conditions are identical with those of run Nos. 7 and 8.

The ash of run No.9 was milled in a ball mill prior charging to the pilot filter. The calcium utilization is not better than in other comparable runs.

Future Work

More experiments on both bench and pilot scale are required in order to get more insight into the governing mechanisms.

CONCLUSIONS

- Furnace limestone injection is a technically available process. It may be applied to boilers which burn fuels having a relatively high water content.
- In a commercial furnace different limestones are equal active on a weight basis irrespective whether they are calcites or dolomites. In laboratory tests exotic materials like precipitated $CaCO_3$ or very pure marbel showed a considerably lower utilization than ordinary limestones.
- Injection of the limestone together with the overfire air gives the best utilization of the limestone.
- Increase of the air excess above the normal level allows application of LIMB also to furnaces burning higher heating value fuels.
- The cooler the furnace is, the better the results obtained with LIMB are.
- Laboratory experiments show a "normal" dependence of the conversion from the SO_2 concentration and from the residence time (after substraction of the time of calcination).
- For a residence time of 10 seconds there is an optimum temperature at 950°C. Shorter residence times may have a higher optimum temperature.
- Secondary utilization of LIMB fly ash may more than double the utilization of the additive.

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Table 1

INSTALLATIONS WITH FURNACE LIMESTONE INJECTION

PLANT NAME	OWNER	Plant erection year	LIMB install. year	Power rating MW	Heating value lower KJ/kg	Water content %	Ash content %	Sulfur %	Burner type	Soot blowing
Voitsberg No. 2	ÖDK	1956	1982x)	65	10500	32÷38	15÷30	0,4 - 1,5	4 corner	not available
St.Andrä No. 2	ÖDK	1959	1983x)	110	9500-1300	35	15÷25	0,5 - 1,2	4 corner	not available
Voitsberg No. 3	ÖDK	1983	1983	330	10500	32÷38	15÷30	0,4 - 1,5	6 corner	once a day
Cogeneration plant, Graz	STEWEAG xx)	1964	1984	3 x 18	12800	36	12	0,4 - 1,2	4 wall	not available
Riedersbach No. 1	ÖKA xxx)	1969	Jan. 1985xxxx)	55	10400-12000	30	23.5	0,45 - 1,9	4 corner	not available

x) Year of permanent installation
xx) Steirische Wasserkraft und Elektrizitäts AG
xxx) Oberösterreichische Kraftwerke AG
xxxx) permanent if trials are positive

Table 2
CHEMICAL COMPOSITION AND SURFACE AREA OF ADDITIVES

Additive Nr.	A	B	C	D	E	F	G	H	I	J	K
water	0.10	0.02	0.11	0.08	0.02	0.05	0.02	0.38	0.07	0.8	0.0
insoluble (SiO_2)	1.68	1.46	1.01	0.94	1.39	1.39	6.02	17.92	2.85		
CaO	53.36	52.85	38.25	54.15	53.37	48.89	32.37	41.16	52.36	53.7	54.4
MgO	0.72	1.93	14.98	1.09	0.93	4.92	16.61	3.43	1.45	0.3	0.2
Fe_2O_3	0.17	0.17	0.11	0.12	0.05	0.14	0.26	1.07	0.34		
Al_2O_3	0.52	traces	0.14	0.32	0.31	traces	0.33	1.04	0.52		
CO_2	43.14	43.45	45.61	43.42	43.52	43.86	44.37	34.47	41.24	42.0	44.5
SO_3	0.08	0.06	0.07	0.02	0.05	0.05	0.01	0.17	0.30		
Blaine cm^2/g	2432	5097	4307	3825	3723	6120	4307	4732	1580		
	tested in Voitsberg Nr. 2									Laboratory tests only	

Table 3

RESULTS OF VOITSBERG NR. 2 TESTS

Run. Nr.	Additive kg/t of brown coal	Additive Nr.	Flue gas recycle	SO_2 in flue gas ppm	$\frac{Ca+Mg}{S}$	D(A)	ALKU
1	-	-	no	1224	1.75	0.095	0.055
2	70	B	no	1135	3.66	0.307	0.084
3	100	B	no	718.8	6.0	0.427	0.071
5	91	A	no	790.5	4.81	0.348	0.072
7/1	100	E	yes	666.6	5.75	0.552	0.096
9	65	F	yes	983.2	3.21	0.353	0.11
10	92	F	yes	663.8	5.0	0.519	0.104
11	-	-	no	1131	2.0	0.193	0.095
12	88	D	yes	689	5.37	0.498	0.093
14	96	C	yes	634	5.8	0.488	0.084
16	90	G	yes	712	5.6	0.432	0.077
18	94	H	yes	709	4.94	0.392	0.079
20	93	I	yes	837	4.39	0.313	0.071

Table 4

UTILIZATION OF ADDITIVE G AT ST.ANDRÄ NO. 2 WITH DIFFERENT METHODS OF ADDITION

Plant load 90 MW (plant rated power = 110 MW), SO_2-concentration 530-800 ppm

Additive G

dropped on conveyor belt		injected with overfire air	
Run No.	ALKU %	Run No.	ALKU %
2	5.5	17	8.72
3	5.7	18	9.25
4	5.3	23	8.32
5	5.5	27	9.38
7	5.28	31	9.84

Table 5

ASH ANALYSES FROM LIMB-FILTER, COGENERATION-PLANT GRAZ 1983

	Run number of LIMB-FILTER					
	5	7	8	9	10	LIMB ash
SiO_2	27.92	35.94	28.70	30.32	30.35	
R_2O_3	20.86	26.32	21.99	22.32	23.01	
CaO	24.26	21.19	27.47	27.70	27.33	26.94
MgO	3.09	1.56	2.31	2.76	2.20	1.17
SO_3	9.73	7.93	8.73	8.11	6.85	3.65
Loss on ignition	11.65	6.18	9.15	8.07	8.84	2.78
H_2O	1.77	0.29	0.39	0.32	0.34	-
	99.28	99.41	98.74	99.60	98.92	
Calcium-Utilization	0.24	0.26	0.222	0.205	0.175	0.095
Ash kg	11	12	12	12	12	
Run-Time hours	41	24	26	25	13	
Treatment	2kg ash milled			milled		
Fluidiz. prim. (spout)	steam	steam	steam	steam	air	

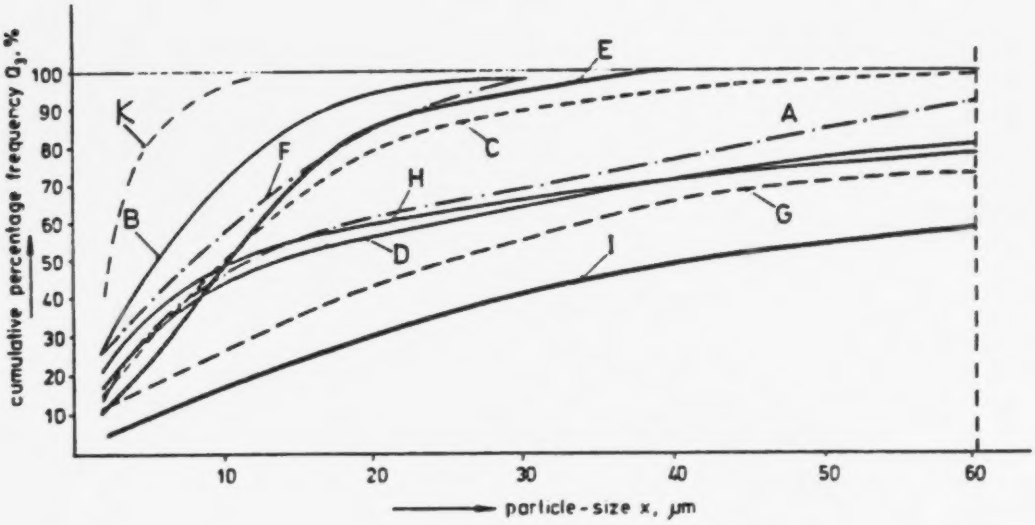


Figure 1 Particle-size-distributions of the used additives

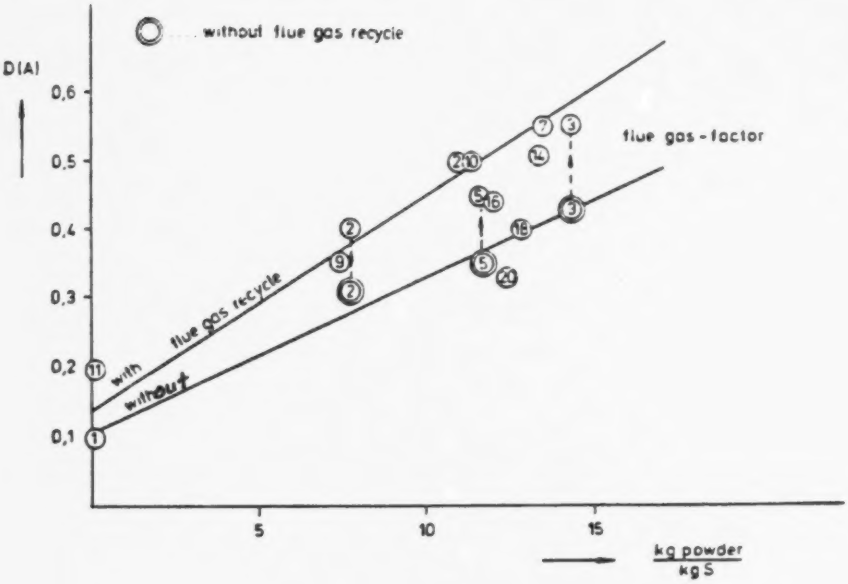


Figure 2 Desulfurization (A) as a function of powder/sulfur ratio

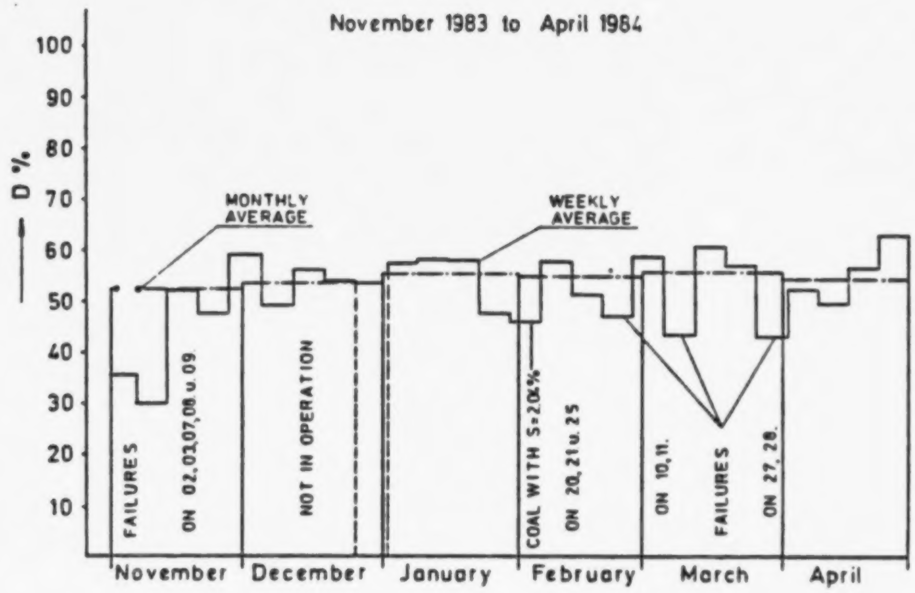


Figure 3 Desulfurization through LIMB in Voitsberg No.3

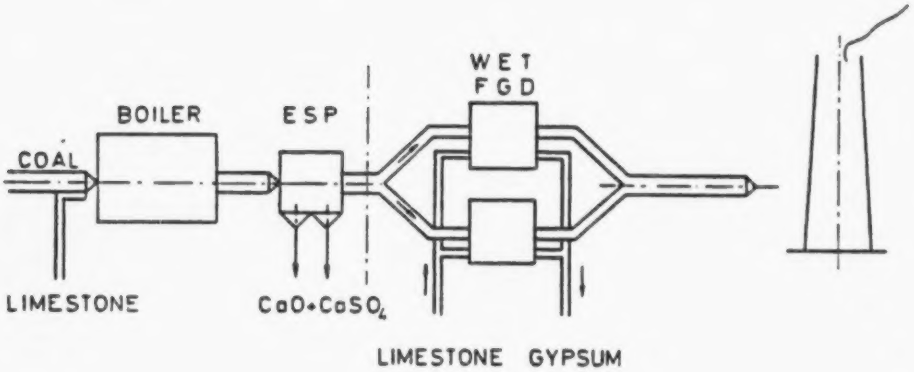

COAL
LIMESTONE
BOILER
ESP
$CaO+CaSO_4$
WET FGD
LIMESTONE
GYPSUM

Figure 4 Desulfurization in Voitsberg No.3

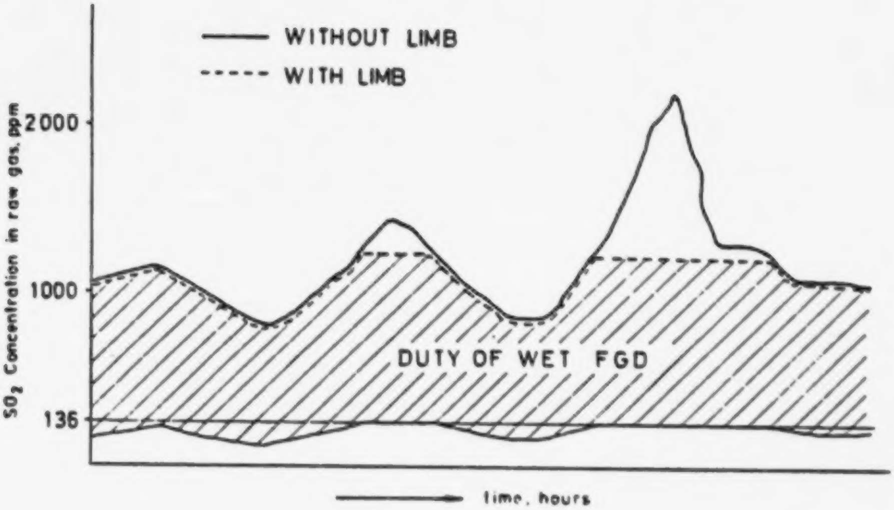


Figure 5 SO_2 Concentration in raw gas with and without LIMB in Voitsberg No.3

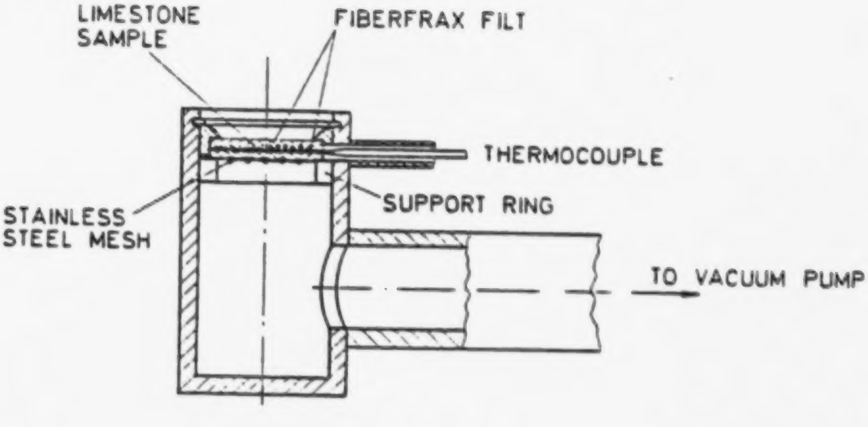

LIMESTONE SAMPLE
FIBERFRAX FILT
THERMOCOUPLE
STAINLESS STEEL MESH
SUPPORT RING
TO VACUUM PUMP

Figure 6 Pipe for holding limestone sample

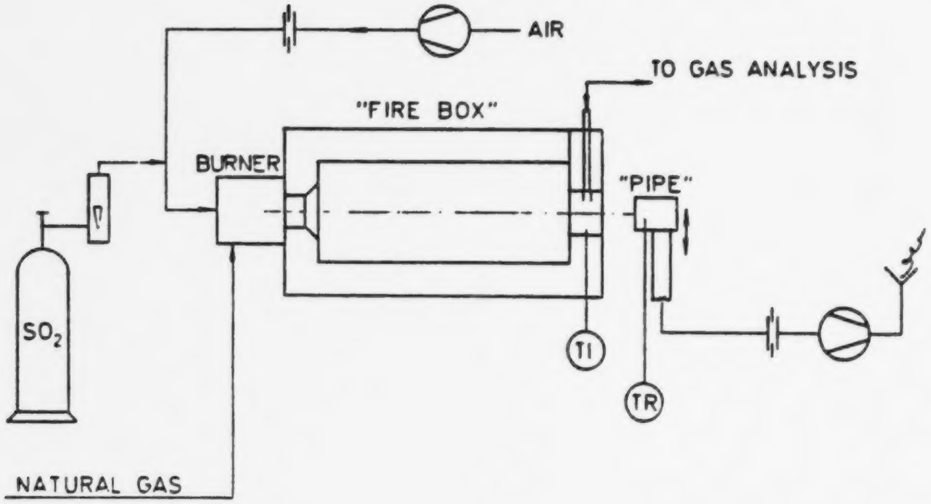
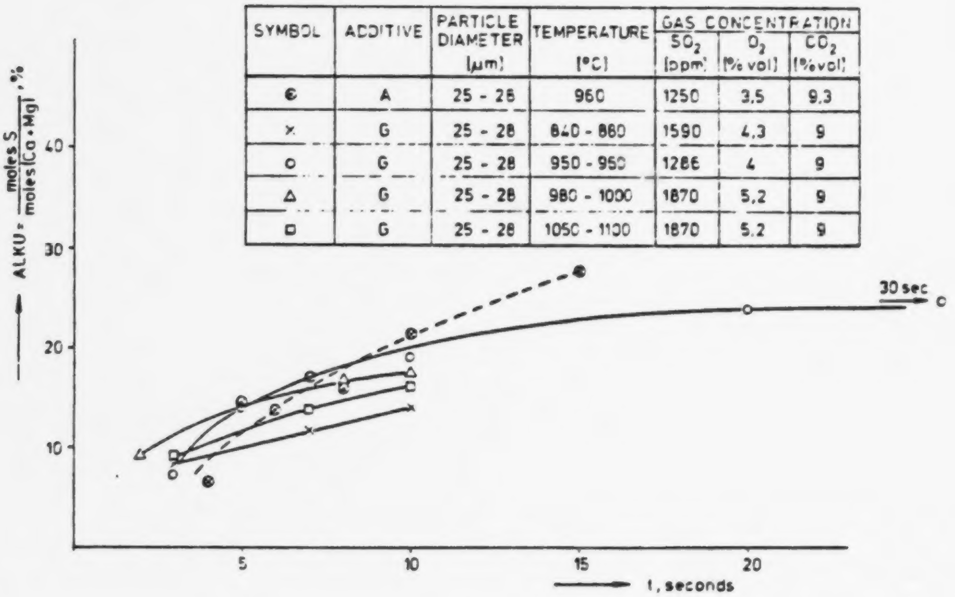
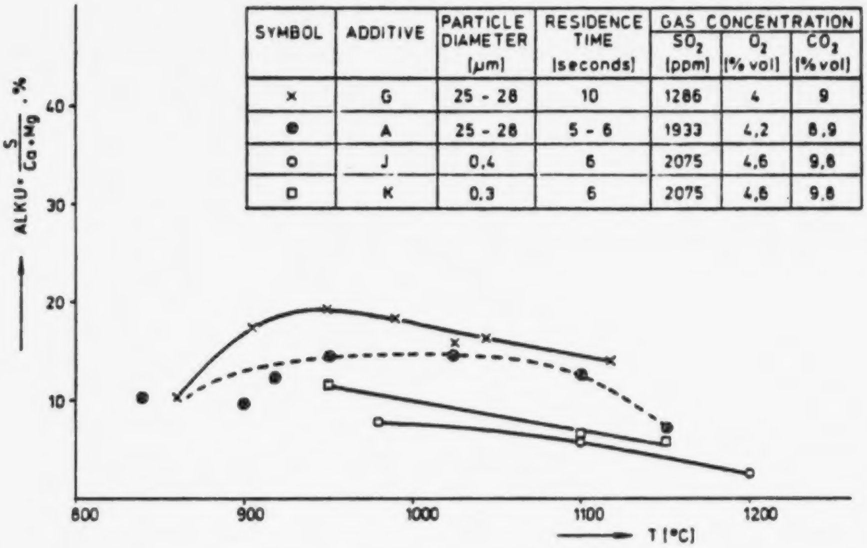

AIR
TO GAS ANALYSIS
"FIRE BOX"
BURNER
"PIPE"
SO_2
TI
TR
NATURAL GAS

Figure 7 Laboratory setup for sulfation of limestone



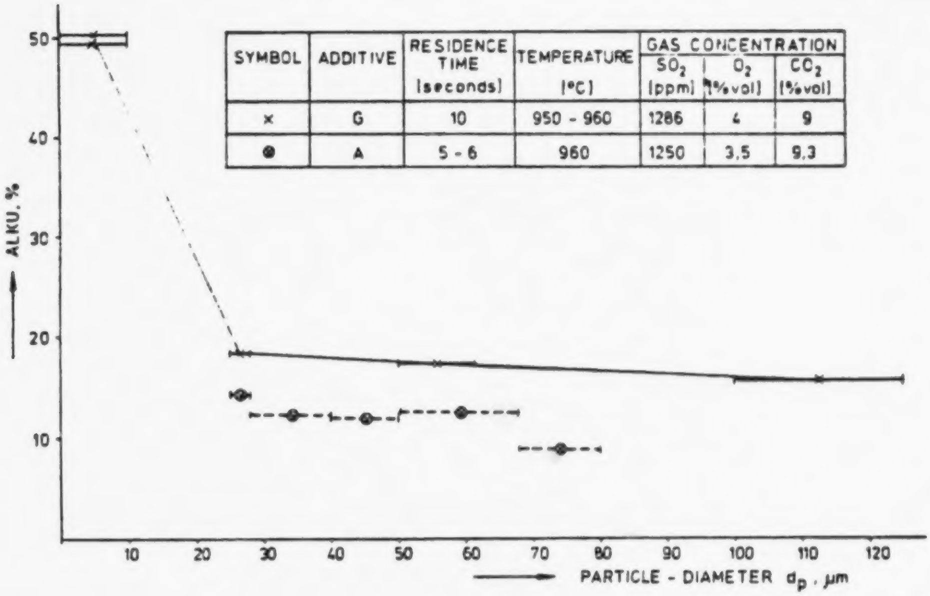
SYMBOL	ADDITIVE	PARTICLE DIAMETER [µm]	TEMPERATURE [°C]	GAS CONCENTRATION SO_2 [ppm]	O_2 [% vol]	CO_2 [% vol]
⊗	A	25 - 28	960	1250	3,5	9,3
×	G	25 - 28	840 - 880	1590	4,3	9
○	G	25 - 28	950 - 950	1286	4	9
△	G	25 - 28	980 - 1000	1870	5,2	9
□	G	25 - 28	1050 - 1100	1870	5,2	9

Figure 8 Conversion of limestone as a function of time



SYMBOL	ADDITIVE	PARTICLE DIAMETER [µm]	RESIDENCE TIME [seconds]	GAS CONCENTRATION SO_2 [ppm]	O_2 [% vol]	CO_2 [% vol]
×	G	25 - 28	10	1286	4	9
●	A	25 - 28	5 - 6	1933	4,2	8,9
○	J	0,4	6	2075	4,6	9,8
□	K	0,3	6	2075	4,6	9,8

Figure 9 Conversion of limestone as a function of temperature



SYMBOL	ADDITIVE	RESIDENCE TIME [seconds]	TEMPERATURE [°C]	GAS CONCENTRATION SO_2 [ppm]	O_2 [% vol]	CO_2 [% vol]
×	G	10	950 - 960	1286	4	9
●	A	5 - 6	960	1250	3,5	9,3

Figure 10 Conversion of limestone as a function of particle size

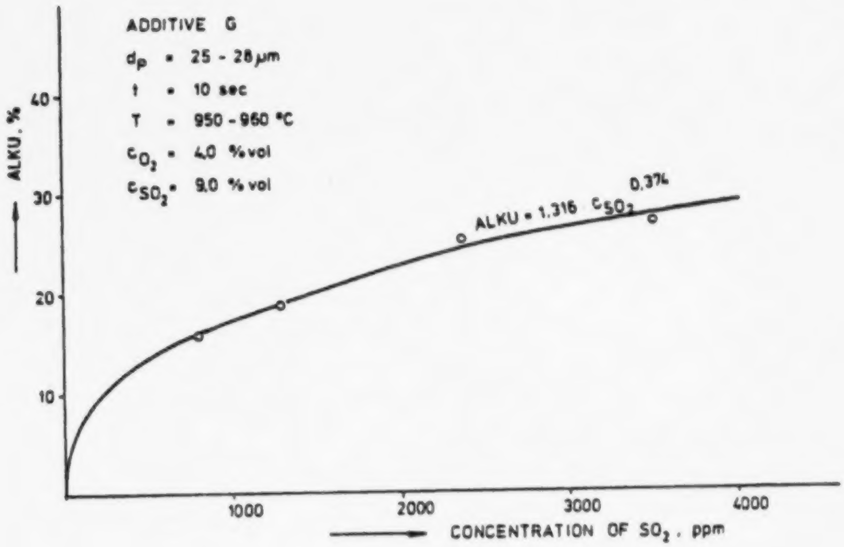


Figure 11 Conversion of limestone as a function of SO_2 concentration

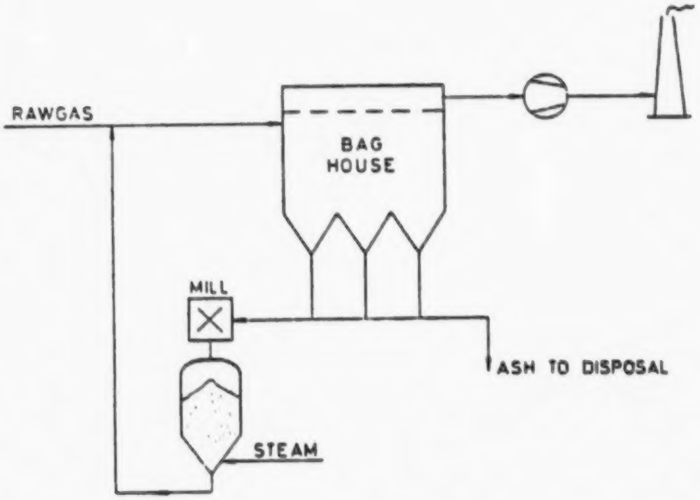

RAWGAS
BAG HOUSE
MILL
ASH TO DISPOSAL
STEAM

Figure 12 LIMB-Filter Process

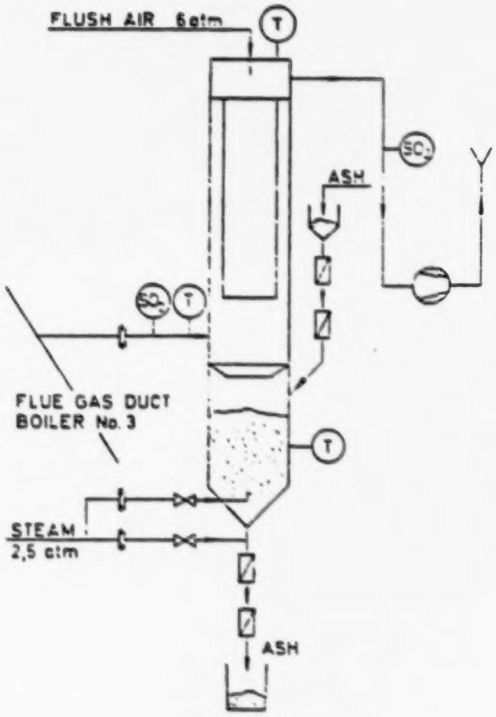

FLUSH AIR 6atm
T
SO_2
ASH
SO_2
T
FLUE GAS DUCT
BOILER No. 3
T
STEAM
2,5 atm
ASH

Figure 13 LIMB-FILTER experimental plant

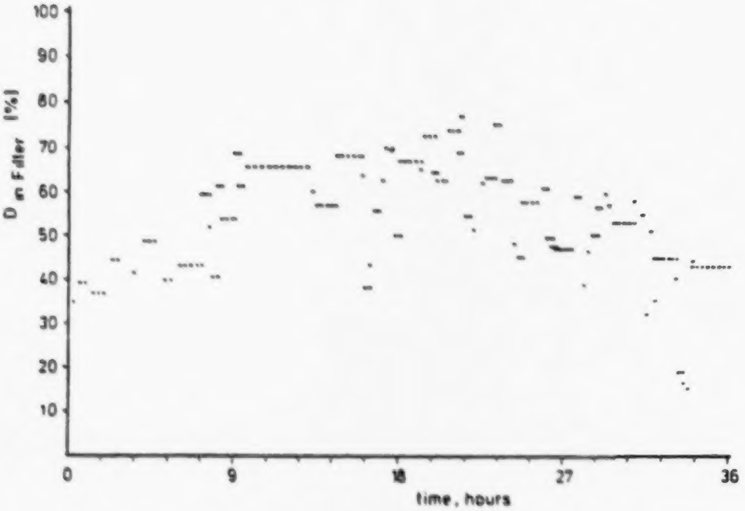


Figure 14 DESULFURIZATION (%) in filter, run No.5

EXPERIENCE WITH FURNACE INJECTION OF PRESSURE HYDRATED LIME AT THE 50-MW HOOT LAKE STATION

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Verlin Menze
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ABSTRACT

A series of tests was recently completed at a 50-MW power plant to evaluate direct furnace injection of pressure hydrated lime to reduce sulfur dioxide emissions. Both high calcium and dolomitic limes were evaluated over a range of injection rates. The sorbents were injected at selected points above the burners in the radiant sections of the boiler. Temperatures in these sections ranged from about 2,000° to over 2,500°F. The low-sulfur lignite fired was from the Beulah mine in North Dakota. The boiler, Hoot Lake Station, Unit 2, was a tangentially fired, balanced draft unit equipped with an electrostatic precipitator for particulate emission control. The burners were operated within normal ranges except in one test with a low NO_x configuration. Some 30 short-term tests were conducted, typically 2 to 4 hours in duration. The tests also included injecting hydrated lime for a continuous 30-hour period to evaluate longer term effects on boiler performance.

This report presents preliminary results of sulfur reduction and calcium utilization. Sulfur reduction values are based on sulfur dioxide measurements in the gas stream. The simple pneumatic system, used to inject the dry sorbents is also described. The results are compared to those from an earlier test series at the station evaluating limestone as the sorbent. Impacts on the performance of the boiler and precipitator are briefly described.

INTRODUCTION

The reduction of stack gas sulfur dioxide emissions by direct injection of calcium compounds into the furnace chamber has been under investigation for over 30 years. In general, the results of these tests indicate that although high sulfur dioxide removals could be achieved, the corresponding sorbent requirement was very high (1,2). There were also potential problems with slagging, fouling, and collectibility of the resulting fly ash sorbent particulate matter. The high additive rates requirements were due to:

- Inadequate residence time of the sorbent particles in the temperature region where sorbent-sulfur dioxide reactions are favored;
- Deadburning (sintering) of the sorbent surface, reducing otherwise available reactive surface area;
- Infraction (intimate mixing of molten ash and sorbent) to deactivate the sorbent; and
- Inferior sorbent characteristics, including large particle size, low porosity, and low specific surface area.

Recently, burner modifications that reduce flame temperatures to reduce nitrogen oxide emissions have been developed that partially overcome some of the above problems. As a result, greater opportunity for increased sorbent utilization has presented itself, i.e., less dead burning when the sorbent is injected directly into the burner zone(s). Residence times have also increased due to more conservative, larger, modern boiler designs. Therefore, under certain site specific constraints, a successful dry sorbent process may present an economically attractive alternative to more conventional processes. Potential advantages include:

- Simplicity, size, and cost of equipment.
- Ease of backfitting existing plants.
- Production of dry solid waste (a dry-to-dry process).
- Reduced water requirements.
- Limited impact on boiler operation/equipment.
- Increased thermal efficiency.

Potential disadvantages include:

- Increased particulate emissions.
- Increased boiler slagging.
- Increased boiler fouling.
- Lower sorbent utilization.

A dry sorbent process being investigated by the Department of Energy (DOE) is the direct injection of pressure hydrated lime. The hydrate is injected into the upper radiant sections of the furnace where it dehydrates and reacts with sulfur oxides in the gas. Temperatures are well below those in the combustion flame or its vicinity, but yet sufficiently high to favor the reaction of sorbent with sulfur dioxide. Deadburning (sintering) and ash deactivating effects can be minimized at optimized injection sites while still providing adequate residence times. The work here is part of a simultaneous SO_x/NO_x emission control project being investigated by the University of North Dakota Energy Research Center (UNDERC) sponsored by the DOE. The sorbents of choice for SO_x control were pressure hydrated dolomitic and high-calcium limes.

Pressure hydrators are commonly used by industry to fully hydrate dolomitic quicklime. Dolomitic lime contains a high proportion of magnesium oxide, resistant to hydration at atmospheric conditions. The pressure vessels are generally operated at pressures ranging from 100 to 150 psig and temperatures ranging from 200° up to 300°F. Temperatures and pressures are produced autogeneously in the sealed vessel due to the heat generated by the hydration reaction. When the hydrated material is released from the pressurized vessel, the particles typically have a diameter of less than 1 micron with high surface area (over 15 m^2/g). Nondolomitic, high-calcium quicklimes hydrated in similar fashion in the laboratory can have similar properties. Pilot plant results (4) indicated that 40 percent sorbent utilization or better could be readily achieved at reasonable stoichiometric ratios (Ca/S near 1.0). The sorbent particle size was in that instance approximately 0.4 microns. Encouraged by the pilot plant results, plans were developed to continue the investigation at a suitable full-scale operating boiler.

EXPERIMENTAL

A field test was conducted at a 50-MW western boiler to evaluate direct injection of pressure hydrated lime to reduce sulfur dioxide emissions. This paper presents the preliminary results obtained during the field test, and includes a comparison of the preliminary data to prior results obtained in 1982 by injection of limestone. In both instances, the tests were conducted at the Hoot Lake Station, Unit 2, operated by the Otter Tail Power Company. The station fires a low sulfur North Dakota lignite from the Beulah Mine of the Knife River Coal Company. The present tests were conducted from September 26, 1984, to October 13, 1984. Thirty-two (32) tests in all were conducted. These included a period when a high calcium hydrate was injected continuously for 30 hours. In five of the tests, a magnesium-containing dolomitic hydrate was employed, also for comparative purposes. In all tests, the sorbent was injected into the furnace above the tangentially fired burners.

The main components of the field test included:

1.0 Injection system optimization.

2.0 Determination of SO_2 reduction and lime utilization rates.

3.0 Evaluation of the effects on electrostatic precipitation performance and particulate emissions.

4.0 Measurement of boiler performance effects in terms of operation, fouling, draft losses, and efficiencies.

5.0 Characterization of sorbent and sorbent-ash mixtures, particularly in view of sorbent's commercial origin.

This report discusses preliminary results obtained in meeting the first two objectives, and are presented without detailed analytical analyses of samples collected during each test series. Therefore, the final data points may be slightly different from the preliminary results presented in this report; however, the numerical magnitude and trends are considered representative. The final report (prepared by EERC) is expected to be completed by May, 1985. Some observations and data gathered in meeting the last three objectives will be briefly highlighted.

Sorbent Injection System. The sorbent injection system specifically designed for the testing at Hoot Lake Unit 2 is pictured in Figure 1. Key features of the injection system included:

- Hydrate storage.
- Feed rate control and turndown (10:1).
- Variable injection site selection.
- Variable injection velocity.

Pressure-hydrated lime was delivered in 1-ton bulk bags for storage on site. Approximately 200 bags in all were delivered, each bag numbered and tared. As required, hydrated lime from the bulk bags was dumped into a 250-cubic foot day storage hopper using a forklift truck. The hopper was equipped with a vibrating bottom to facilitate flow of the material. Due to fluctuations in the density of the lime, the original screw feeder produced erratic flow rates during the initial tests. The screw feeder was replaced with a digitalized weigh feeder, which provided accurate and constant feed rates. Feed rates were also measured by the known weight of material added to the hopper for comparison to the weight feeder.

From the feeder, the lime flowed through a rotary airlock to a pneumatic conveying line. During the tests, lime feed rates were varied from 400 to 4,400 lbs/hr. Conveying air was supplied to the system at up to 120 inches static pressure from a rented compressor. Air flow ranged up to 1,400 scfm. The material flowed through the 6-inch diameter line, to the primary splitter located on the second level of the power station. From the primary splitter, the flow was further split by a pair of secondary splitters. As originally installed, as shown in Figure 1, four flexible injection lines were used to shoot the lime into the furnace gas. Later, an additional splitter was added to further split one-half of the flow into four parts. This gave a six-nozzle delivery system. The pipe nozzles were readily replaced to vary injection velocities from 200 to 300 fps. Three nozzle sizes were available: a 1.56-inch round, a 2.06-inch round, and a 1.0 by 2.44-inch rectangular. Via these nozzles, sorbent was fed through available observation doors, over-fire air ports, and other ports at various levels of the furnace as indicated in Figure 2. Although a temporary installation, many features and operations would be similar in a permanent one.

PRELIMINARY TEST RESULTS

After a series of shakedown runs to test the sorbent system's operability and the analytical testing procedures, testing commenced on September 26 and was completed on October 13, 1984. Pressure hydrated high-calcium and dolomitic sorbents were tested. The actual testing proceeded in a series of four phases, differentiated by their objective(s):

- Injection system optimization, using four nozzles at 44 or lower MWG.
- Improved sorbent dispersion, using six nozzles at 44 MGW.
- Impact of varied Ca/S ratios, by varying the sorbent injection rates.
- Longer term effects during thirty-hours of continuous injection.

The initial test phase was dedicated to the optimization of injection locations and nozzle geometry. Initially, sorbent was injected through four nozzles at individual levels of the furnace (at levels 3 or 4 or 5) to evaluate temperature and dispersion effects. The plant maintained a constant generating load of 44 MWG with the top level of burners out of service. This gave a heat release rate of 15,000 Btu/ft^3 hr in line with current U.S. boiler standards. Under these conditions sulfur reduction ranged from about 20 to about 49 percent when the Ca/SO$_2$ mole ratio was varied from 1.5 to 3.5, as shown in Figure 3. Calcium utilization rates were unexpectedly low, as shown by the dashed line in Figure 4. However, sulfur dioxide content of the gas was also low, ranging from about 500 ppm to 700 ppm, corrected for dilution. At concentrations below 1000 ppm, utilization rates can drop drastically. Sulfur analysis of the lignite fired at the time of 0.55 to 0.76 percent confirmed the lower than expected SO$_2$ measurements. (The typical lignite at the plant ranges about 1.1 percent in sulfur content.)

Results while injecting entirely on the fourth floor (four nozzles) appeared superior to those at the other two levels (corresponding to different injection temperatures) at constant load. This is illustrated in Figure 3 where flue gas sulfur dioxide reduction (%) results tend to fall about the lower dashed line during the initial tests. Injection on the fifth level front produced an exceeding poor result falling well below the line due to poor sorbent distribution. Results at Level 3 were average or below. At the tail end of the initial tests, an additional two tests were conducted while the burners were fired in a "low NO$_x$" configuration. Temperatures were reduced in the furnace. Sulfur reduction values did improve to a modest degree falling about the upper dashed line of Figure 3. Calcium utilization rose to near 18 percent at a stoichiometry near 3.0. In general, however, SO$_2$ removal efficiency and sorbent utilization values were significantly below expectations based on pilot plant studies. This was also the case in the few tests conducted at still lower loads (34-38MWG). Visual observation of the sorbent streams in the furnace, indicated that sorbent dispersion in the flue gas was not optimal. Therefore, a six nozzle system was devised in an attempt to achieve better dispersion. Subsequent analyses of the hydrated material indicated that varying sorbent properties may also have contributed to the low removal efficiencies in the initial tests.

The six nozzle system was evaluated at various furnace levels, including the sixth as well as the fourth and fifth levels. Simultaneous injection at several levels was the norm. Seven different configurations were investigated at a nominal constant stoichiometric ratio ranging from 1.4 to 1.7. Also, during this period, a digital weigh feeder replaced the screw feeder to obtain better control of sorbent feed. Sulfur reduction was improved over the earlier tests, as illustrated by the cluster of data points falling on the higher solid line shown in Figure 3. Some partial evidence also suggests sorbent properties may have simultaneously improved as well. Calcium utilization values also clustered about the mid to upper 20 percent levels, at an appoximate stoichiometric ratio of 1.5, as shown in Figure 4. Of the configurations investigated, the more successful appeared to be those which included injection at the rear of the fourth level. This provided treatment of the gas tucking under the pendant superheater. Other than this observation, no real differences in results were apparent among the various configurations so the tests continued with injection both on the fourth (two nozzles) and fifth floors (four nozzles). This injection configuration was a compromise between considerations of residence times versus excessive temperatures. Using this configuration, the tests continued to the key objective of determining the effectiveness of varying sorbent rates on sulfur reduction.

Injection rates were systematically varied to produce molar Ca/SO_2 ratios ranging from 0.5 to 4.7. Sulfur reductions increased in a near monotonic progression from about 22 percent up to 73 percent, with increasing molar ratio. The data falls about the upper solid line in both Figures 3 and 4. Near a molar ratio of 2.0, a 50 percent sulfur dioxide reduction was observed, resulting from a 25 percent utilization of the hydrated lime. It is also shown that somewhat improved results were obtained using dolomitic lime. These are presented in the uppermost dashed line in Figures 3 and 4. However, since the dolomite contains 45 percent unreactive magnesium oxide, about twice the weight of material must be used to give equivalent molar ratios of calcium to SO_2. Boiler operations and economics, therefore, may favor the high calcitic hydrated lime.

At the conclusion of the feed rate parametric testing, a 30-hour test was initiated to confirm SO_2 removal efficiency data, to identify operational problems, and to characterize the impact on ESP operation. During the extended period of injection, sulfur content in the lignite varied from about 0.6 to 0.9 percent, increasing baseline sulfur dioxide levels. Also, sodium levels in the coal doubled from 4.8 to 9.6 percent. Soot blowing was increased to levels normal for the high sodium content. As sorbent injection continued, controlled sulfur dioxide concentrations fell to 280 ppm, equal to about a 67 percent reduction at a Ca/S ratio of about 2.7. The preliminary results are presented as a star in Figures 3 and 4, and are approximately comparable to the best results obtained with the dolomitic hydrate. Possible explanations for the higher SO_2 removal efficiency compared to the parametric data include: 1) Coal sulfur levels rose above those in any other test; 2) Sorbent properties improved, i.e., particle size, specific surface area and porosity; 3) Dynamic buildup of the sorbent on furnace tubes continually presenting reactive surfaces for sulfur dioxide capture. Differentiating among any of these or other possibilities is beyond the scope of our preliminary discussion here.

LIMESTONE INJECTION COMPARISON

Seven tests were conducted at the Hoot Lake Station in 1982 (2) to determine the effectiveness of SO_2 removal using limestone injection. The limestone was injected either with the lignite through the burners, i.e., pulverized with the coal, or directly into the furnace at the fourth level. A -200 mesh material was used for the direct injection. The boiler was operated at 44 MW with the top row of burners out of service as in the present tests. Most of the 1982 tests were conducted with a low NO_x burner configuration employing the burner-out-of- service (BOOS) method.

During the 1982 series, the Ca/S (injected limestone to coal sulfur) mole ratios varied from 1.6 to 5.0 while apparent SO_2 removal (based on flue gas analysis) increased from 21 to 47 percent. Note that the mole ratio is different from that used in the present study. Results from the present test were thus converted to the same basis for comparison and are illustrated in Figures 5 and 6. The lower line depicts the limestone data; the upper two lines, the band of SO_2 removal data obtained upon injection of the hydrated lime. As the hydrated lime Ca/S (coal) mole ratio was varied from about 0.4 up to about 4.2, sulfur removal efficiency ranged from about 16 up to about 83 percent, as shown in the banded data. At a stoichiometric ratio of about 1.6, the limestone achieved only a 21 percent sulfur removal; the pressure hydrated lime at the same stoichiometry removed 40 to 55 percent of the flue gas sulfur dioxide, a 90 to 160 percent improvement. The dolomitic hydrate appears even more effective, removing about 65 percent of the sulfur dioxide at the same stiochiometric ratio. High calcium hydrated lime in the 24-hour test gave comparable results to the dolomitic hydrated lime.

The greater effectiveness of the hydrated limes is also demonstrated in terms of calcium utilization presented in Figure 6. At the lower Ca/S ratios, 1.6 and below, utilization of the lime sorbent was two to three times that of the limestone. To reduce sulfur dioxide concentrations by 50 percent required a Ca/S mole ratio greater than 4.7 with the limestone. With the pressure hydrated lime, the Ca/S mole requirement was about 1.8 based on coal sulfur content. On a weight basis, over three times the amount of limestone must be injected in comparison to the hydrated lime. This will of course have significant economic impact on operating costs.

PLANT OPERATIONS

Boiler Performance. Boiler operation during the tests was continuously monitored by plant and EERC personnel. The data collected has yet to be analyzed in any quantitative manner. Qualitatively, however, it was observed that there was no significant impact on boiler performance related to the sorbent injection. Soot blowing schedules, if at all, were curtailed so as not to interfere with test measurements. Due to the rise in sodium in the coal during the 30-hour injection phase, soot blowing frequency was increased to a schedule normal for high sodium situations. No significant increase in draft losses was noted.

Fouling probe data has been partially analyzed indicating an approximate doubling of the fouling rate. Deposits, however, were soft and fluffy, readily removed by soot blowing. In areas not accessible to the blowers, deposit growth appeared limited, sloughing off the tubes once growth (weight) exceeded adhesive forces. High sodium conditions apparently aggravated the situation. Nevertheless, the plant operators through normal procedures were able to control boiler temperatures and pressures within their normal operating ranges. More quantitative results await further data reduction.

Precipitator Performance. Impact on precipitator performance was evaluated by two means:

- Observation of the existing precipitator in terms of power levels, resultant stack opacity levels, and in the 24-hour test phase by the determination of collection efficiency. Particle size distributions of the sorbent-fly ash mixtures were also determined by Anderson cascade impactors to estimate fine particulate penetration.
- Determinations of resistivity and ability to improve performance by conditioning the ash with moisture and/or sulfur trioxide using a slip stream of the flue gas.

Without any optimization of the precipitator controls, opacity levels read from the plant transmissometer during the entire test phase never exceeded 10 percent, well below the 20 percent NSPS requirements. Stack appearance remained essentially clear. In the four-field precipitator, power levels in the first field decreased by about 6 to 7 percent. This was due to the slight current suppression effect caused by the increased loading. Power stood constant in the remaining three fields. In this case of a high sodium fly ash (sodium enhances conductivity), resistivity never exceeded 10^9 ohm-cm. Some representative values are given in Table 1. Any attempted conditioning of the already low-resistivity ash failed to make any significant reduction in resistivity. The advantage of reduced sorbent addition, therefore, also accrued to the precipitator's control function. In contrast, during the 1982 tests with high rates of limestone addition, opacity levels did approach 20 percent.

CONCLUSION

The preliminary results of this field test indicate that 50 pct. removal of SO_2 at calcium-to-sulfur ratio of 2.0, corresponding to a calcium utilization of 25 pct can be achieved. Sulfur capture and utilization rates in this test series were superior to those demonstrated at the station in an earlier 1982 test series evaluating injection of limestone.

ACKNOWLEDGEMENTS

We wish to acknowledge the outstanding cooperation of the people of the Otter Tail Power Company. These include Robert Middleton, Director, Production Operations; Robert G. Johnson, Manager, Steam Generation; and Norman Ringstrom, Plant Manager, Hoot Lake Station. Roy Payne, EERC, is also to be thanked for his critical insights and guidance in furthering the work here.

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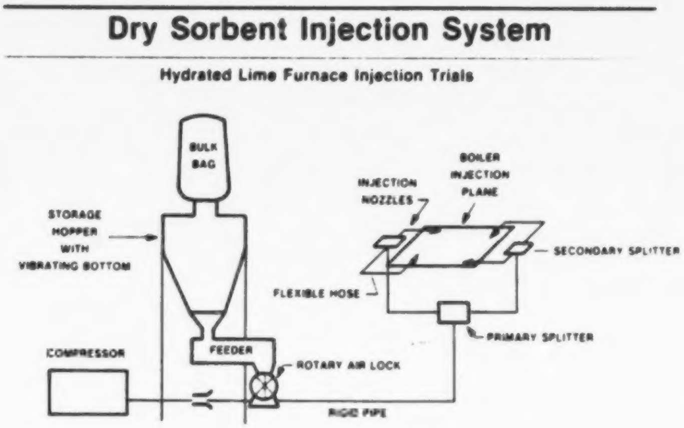
Dry Sorbent Injection System
Hydrated Lime Furnace Injection Trials
BULK BAG
STORAGE HOPPER WITH VIBRATING BOTTOM
INJECTION NOZZLES
BOILER INJECTION PLANE
SECONDARY SPLITTER
FLEXIBLE HOSE
PRIMARY SPLITTER
COMPRESSOR
FEEDER
ROTARY AIR LOCK
RIGID PIPE

Figure 1. Dry Sorbent Injection System

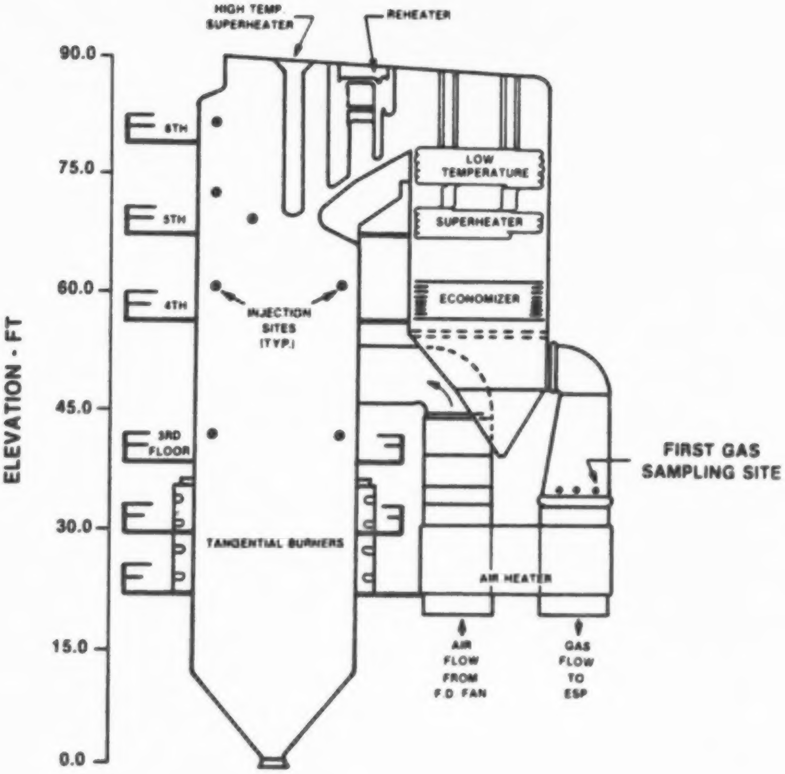
HIGH TEMP. SUPERHEATER
REHEATER
ELEVATION - FT
90.0
75.0
60.0
45.0
30.0
15.0
0.0
6TH
5TH
4TH
3RD FLOOR
LOW TEMPERATURE
SUPERHEATER
ECONOMIZER
INJECTION SITES (TYP.)
FIRST GAS SAMPLING SITE
TANGENTIAL BURNERS
AIR HEATER
AIR FLOW FROM F.D. FAN
GAS FLOW TO ESP

Figure 2. Elevation of Hoot Lake Unit 2

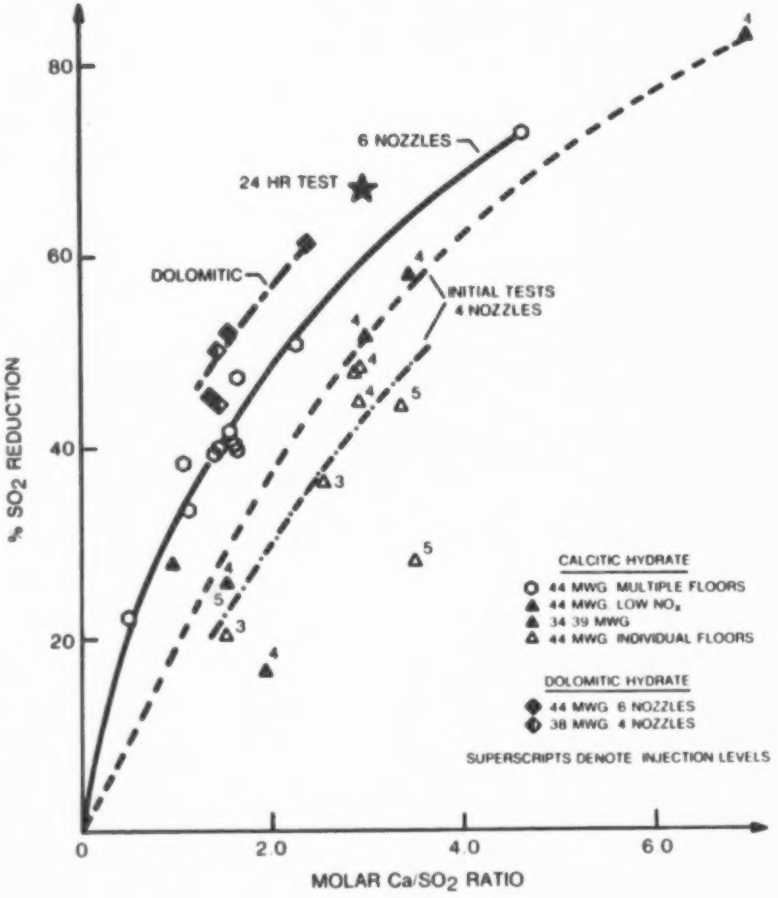

Figure 3. SO_2 Reduction By Pressure Hydrated Lime As Sorbent Feed Rate Was Varied

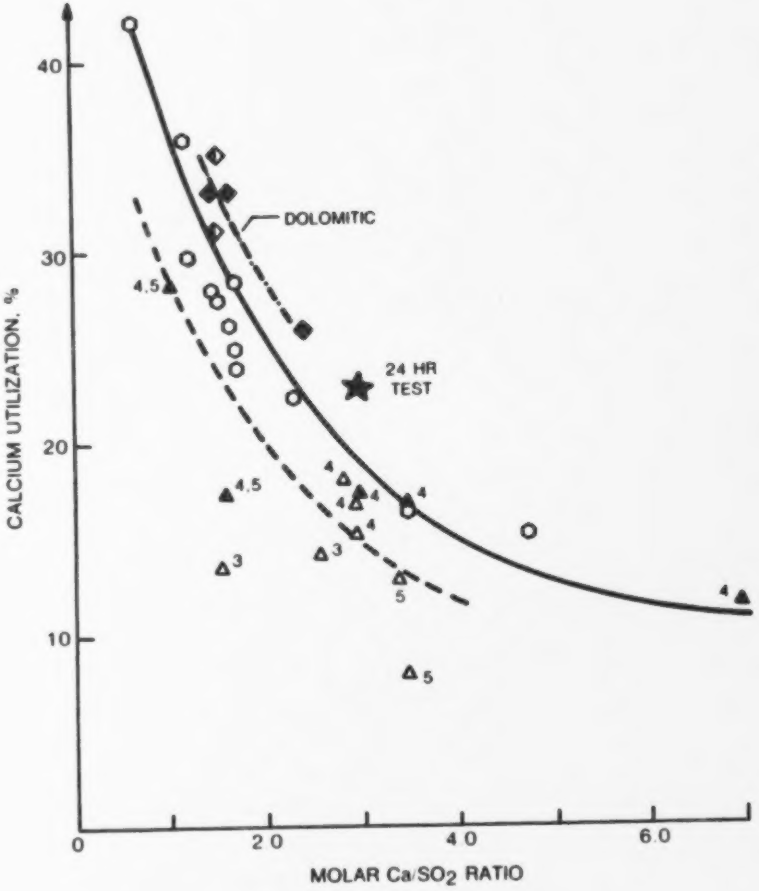

Figure 4. Calcium Utilization As Sorbent Feed Rate Was Varied

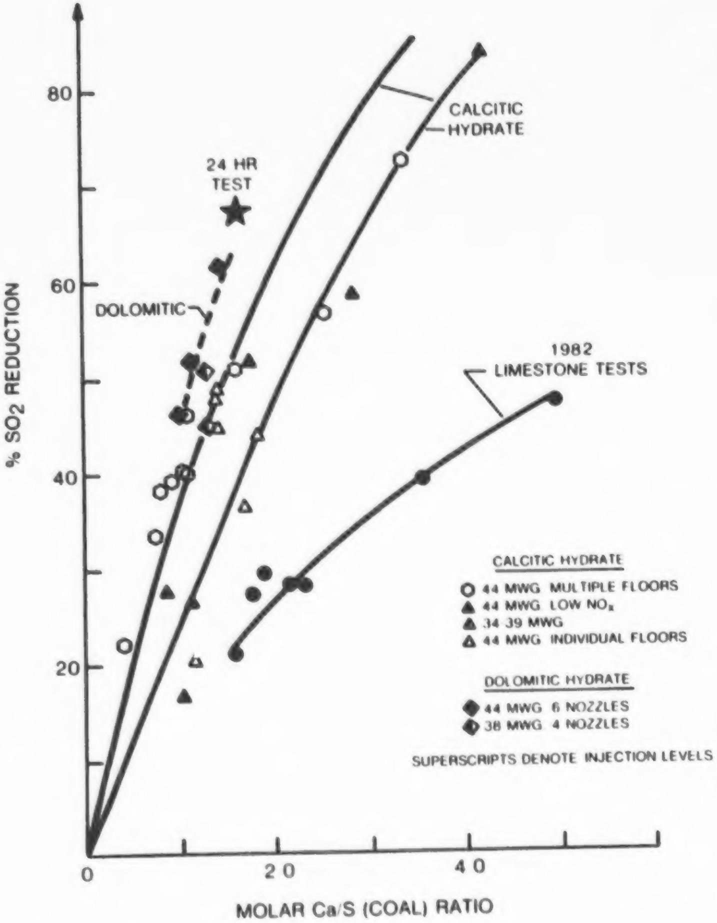

Figure 5. SO_2 Emissions - Pressure Hydrated Lime Compared To Limestone Trials In 1982 (2)

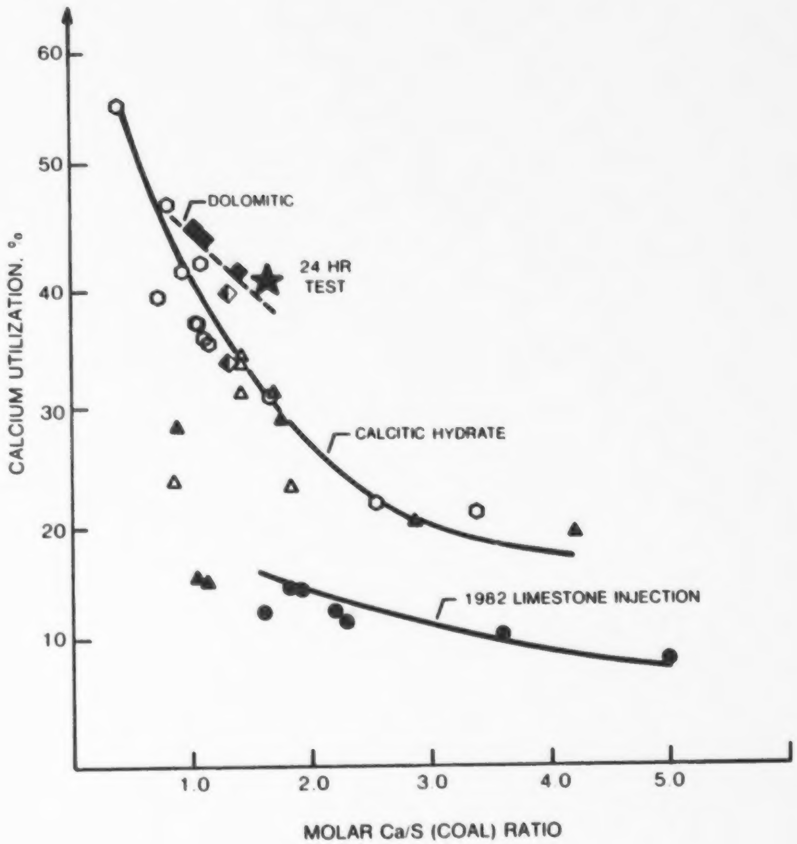

Figure 6. Calcium Utilization - Pressure Hydrated Lime Compared To Limestone Trials In 1982 (2)

Table 1

IN-SITU RESISTIVITY RESULTS
EXTENDED TEST PERIOD OCTOBER 11-13, 1984
Precipitator Slip Stream

Date	Time	Sorbent lb/hr	Flue Gas Conditioning	Temperature °F	Resistivity ohm-cm
10/11	1050	--	None	350	4.3×10^8
10/11	2220	2,880	None	360	9.2×10^8
10/12	0510	2,520	None	360	8.7×10^8
10/12	0540	2,520	30 ppm SO_3	360	7.9×10^8
10/12	0600	2,520	60 ppm SO_3	360	8.4×10^8
10/12	0630	2,520	Cooling	280	3.5×10^8
10/12	0710	2,520	Cooling	200	3.0×10^8

EPA WALL-FIRED LIMB DEMONSTRATION

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ABSTRACT

The U.S. Environmental Protection Agency is engaged in a research program to develop improved control technologies for emissions of sulfur and nitrogen oxides (SO_x and NO_x) from the combustion of fossil fuels. Previously developed low NO_x systems for coal combustion are being demonstrated, and methods for removal of SO_x in the combustion process in conjunction with these systems are under development.

A low-cost method for SO_x control is the use of Limestone Injection with a Multistage Burner (i.e., low NO_x burner). This technology, abbreviated LIMB, promises to be retrofittable to large and small coal-fired boilers at a lower capital and operating cost than currently available pollution control alternatives such as flue gas desulfurization.

EPA has recently awarded a contract to Babcock & Wilcox (B&W) for a full-scale utility size demonstration of LIMB. This paper describes the recently initiated EPA LIMB Demonstration Project with emphasis on outlining the project objectives and scope and describing the demonstration host site.

INTRODUCTION

Nearly all approaches to meeting the country's energy needs call for an increasing reliance on American coal. But coal burning must be accomplished without compromising the country's environmental goals, necessitating technology which will minimize the environmental impact of coal burning at an acceptable cost to the utility customer.

The U.S Environmental Protection Agency is engaged in a research program to develop improved control technologies for emissions of sulfur and nitrogen oxides (SO_x and NO_x) from the combustion of fossil fuels. These emissions are important because of their magnitude and their apparent link to acid rain. Previously developed low NO_x systems for coal combustion are being demonstrated, and methods for removal of SO_x in the combustion process in conjunction with these systems are under development.

A low-cost method for SO_x control is the use of Limestone Injection with a Multistage Burner (i.e., low NO_x burner). This technology, abbreviated LIMB, promises to be retrofittable to large and small coal-fired boilers at a lower cost than currently available pollution control alternatives such as flue gas desulfurization. The process, if successful, would also enable many existing older power plants to reduce emissions while burning high sulfur coal, which is lower in cost than low sulfur coal which might otherwise be required.

Recently, EPA requested and received proposals for a full-scale utility size demonstration of LIMB. A proposal from Babcock & Wilcox (B&W), a major utility boiler manufacturer located in Alliance, Ohio, was selected for contract award. B&W proposes a 3-1/2 year project that includes design and installation of a LIMB system at Ohio Edison's 105 MW coal-fired Edgewater Station in Lorain, Ohio, and a full year of operating and testing to demonstrate its capabilities. EPA will share the cost of the project with the major project participants - B&W, Ohio Edison, the State of Ohio, Stone & Webster Engineering, and Radian Corporation.

HISTORICAL PERSPECTIVE

Dry sorbent injection was evaluated by EPA in a full-scale demonstration at TVA's Shawnee plant from 1968 to 1971. The general conclusions from that study were that there was insufficient SO_x removal (15-50%), that thermal deactivation (deadburning) of the sorbent and decomposition of the sorbent/sulfur complex were a major problem, and that there was inefficient mixing of sorbent with combustion gases. In addition, power plant operational problems occurred including fouling in the convective passes and loss in electrostatic precipitator efficiency. The technology was put on the shelf until 1979 when EPA pilot plant tests indicated the possibility of 70% removal of SO_x with limestone injection through low-NO_x burners. These tests renewed interest in limestone injection technology and launched EPA into a research program to define reaction mechanisms and identify conditions to optimize the technology.

In recent years, progress has been made on many fronts in understanding sorbent injection technology and resolving problems identified with the use of the technology. The mechanisms and kinetics of sorbent reaction with SO_x have been studied, and the critical importance of an optimum temperature range has been identified. The negative influence of flyash on sorbent utilization has been identified, and methods have been evaluated for minimizing deactivation of the sorbent. Recent EPA research has concentrated on production of highly reactive sorbents which promise to increase sorbent utilization and reduce the quantity of sorbent required. Other studies are evaluating the effects of sorbent injection on flyash characteristics and electrostatic precipitator performance, the effects of injection parameters on sorbent mixing and subsequent utilization, and the effects of boiler design and operation on sorbent reaction conditions.

Full-scale trials of dry sorbent injection are planned or are in progress in the United States and in several other countries which will give further experience with the technology. To mention a few, at Otter Tail Power Company's Hoot Lake Unit 2 in the U.S., lime was injected in a tangential-fired 53 MW boiler burning lignite for a 3-week evaluation of SO_x reduction. Pennsylvania Electric Company is evaluating sorbent injection in a 640 MW wall-fired boiler burning low sulfur cleaned coal. Also in the U.S., Conoco is evaluating sorbent injection in a

15 MW industrial boiler firing a high sulfur coal. In the Federal Republic of Germany, injection tests on a 60 MW utility boiler and a follow-up demonstration at a 300 MW brown-coal-fired boiler have recently been completed. Also in Germany, a demonstration of sorbent injection is now underway on the 700 MW Weiher III tower boiler burning a low sulfur coal. In France, experiments with sorbent injection on a 50 MW tangentially fired boiler have been used to design a system for applying the technique to a new 600 MW boiler. In Austria, six boilers ranging in size from 20 to 330 MW have been evaluated with furnace injection. Finally, full scale limestone trials at Saskatchewan Power in Canada on a lignite fired utility boiler were recently completed.

Based upon an improved understanding of dry sorbent injection technology and the additional experience that can be brought to bear upon the design of an injection system, EPA feels that a demonstration of the LIMB technology on a U.S. coal-fired utility boiler is now timely as a culmination and confirmation of the improved knowledge that has been obtained within the last few years.

LIMB DEMONSTRATION OBJECTIVES

The basic goal of the LIMB Demonstration is to extend the LIMB technology development to a full-scale application on a wall-fired utility boiler. By co-funding such a demonstration with industry, EPA hopes to encourage the acceptance and ultimate commercialization of this technology in the shortest possible time.

The successful retrofit of LIMB to an existing boiler is expected to demonstrate that (a) reductions of 50 to 70% in SO_x and NO_x emissions can be achieved at a fraction of the cost of add-on flue gas desulfurization systems, (b) boiler reliability, operability, and steam production can be maintained at levels existing prior to LIMB retrofit, and (c) technical difficulties attributable to LIMB operation - such an additional slagging and fouling, changes in ash disposal requirements, and an increased particulate load - can be resolved in a cost-effective manner. A more definitive expression of these goals will be developed early in the project to be used to guide project decisions and to measure the success of the demonstration program.

PROJECT TEAM AND FACILITIES

The LIMB Demonstration contract was awarded to Babcock & Wilcox on September 28, 1984, based upon a competitive procurement process. The B&W project team consists of Babcock & Wilcox (project management, injection system design), Ohio Edison (host utility), Stone & Webster Engineering (facilities engineering), Radian Corporation (emission testing), and Energy and Environmental Research Corporation (preliminary LIMB technology selection). The demonstration will be co-funded by EPA, the State of Ohio, and the project team members. The host utility site will be Ohio Edison's 105 MW Edgewater Unit 4 located in Lorain, Ohio. The unit (Figure 1) is a B&W-designed, high-pressure, high-temperature, wall-fired boiler for pulverized coal firing. The unit is presently burning 1.5% sulfur coal but will switch to 3% sulfur coal during the demonstration period.

Major components of the boiler are superheaters, a pendant reheater located in the convection pass, economizers, and air heaters. Water and steam pass through the boiler under natural circulation. The precipitator is typical of precipitators retrofitted to utility boilers in the last 5 years and includes ample collection surface and power supply to enable compliance with particulate requirements when burning low sulfur coals. The power supply and rapper controls offer complete flexibility to examine alternate operating modes so as to more fully characterize the impact LIMB will have on the wide range of equipment installed on utility boilers. A summary of boiler descriptive data is provided in Ta Table 1.

SCOPE OF THE PROJECT

The demonstration project proposed is a 3-1/2 year effort in which a LIMB system will be retrofitted to the Edgewater Boiler No. 4, operated, and evaluated. A project schedule is shown in Figure 2. The project consists of several distinct phases - a preliminary stage to develop the LIMB process design applicable to Edgewater 4, a construction and start-up stage, and an operation and evaluation stage. These stages are more specifically described below.

Preliminary Activities

The preliminary phase of the project is a recognition of the dynamic state of LIMB technology development at this time. On-going LIMB developmental work at EPA and in the private sector is expected to provide resolution of many of the technical issues that affect process design within the time frame required for the specification of the final design for this demonstration. The preliminary phase will enable the contractor to evaluate new work with respect to LIMB retrofit to the host site and to tailor a process design specific to the host site. EPA is expecting to work closely with the contractor during this preliminary activity to participate in specifying the design parameters for the LIMB system to be demonstrated. It is expected that the development of the process design will also involve consultation with major LIMB researchers as well as conduct of limited on-site studies to characterize the boiler and other studies to further refine the selection of LIMB design parameters. On-site studies might include measurement of boiler temperature and velocity patterns, evaluation of boiler structural components, and similar activities. Other limited studies to refine LIMB design parameters might include specific sorbent and coal characterization studies, investigation of deposition and collection characteristics of sorbent/ash mixture, and similar site-specific investigations.

The primary product of this phase will be a preliminary design for a LIMB retrofit to the Edgewater Boiler No. 4. This preliminary design will include a description of key design features, general process description, a process flowsheet, equipment and structural layouts, and a description of other requirements. A cost estimate and a project schedule will also be prepared.

This phase will also enable the contractor to clarify and upgrade the expected performance goals for the demonstration project within the capabilities of the preliminary design. The performance goals will address the expected emission control performance, boiler performance and reliability, boiler operability, and downstream effects.

Upon completion of the preliminary phase, expected by August 1985, a package will be prepared that includes a process design, estimated cost, schedule, and reassessed performance goals. The preliminary package will be evaluated by EPA for technical merit and for assurance that the project goals can be met as proposed within funding available. A go/no-go decision will be made prior to the installation of the proposed LIMB system.

Design and Installation of LIMB Retrofit

Upon approval of the preliminary design concept, the contractor will proceed with the engineering design, installation, and start-up of the LIMB retrofit. Major retrofit components are not yet defined, but the original proposal was based on the following items:

a. B&W Dual Register Burners/Modified Windboxes/Overfire Air Ports

b. Sorbent Handling and Injection System

c. Additional Sootblowers

d. B&W Continuous Gaseous Emission Monitoring Equipment

e. Support Structures, Miscellaneous Equipment

Upon completion of equipment installation and check-out, the system will be operated during a brief optimization period before the test phase begins to examine the various operating alternatives and select the best procedure for the 1-year performance test. These tests will be short-term in nature and will not be analyzed as extensively as the performance tests. It is expected that the system will be available for a performance evaluation by January 1987.

Performance Evaluation

A broad and complete evaluation is required to characterize the performance of the retrofit LIMB system. Because LIMB is an emission control technology, emission characterization is an important aspect of the performance evaluation. However, operational aspects of LIMB must also be determined. For example, we know, based on the Shawnee experience and our experience with LIMB technology of recent years, that LIMB application can:

- Alter the boiler's temperature profile which may impact boiler efficiency.
- Increase the amount of mass loading which may result in convection pass plugging and accompanying draft losses, increased tube erosion, greater sootblowing requirements, and increased particulate emissions.

- Alter the chemical composition of solids going overhead which may result in increased furnace slagging, tube corrosion, and decreased ESP performance.

- Potentially affect the solid waste disposal requirements, since increased solid wastes with a different chemical composition will result.

To quantify these and other effects, a two-part program has been devised to provide a full characterization of the LIMB retrofit. A baseline test will be made early in the project to quantify and document normal operations that occur in the absence of LIMB. The baseline test will include a rigorous test program of on-site measurements coupled with an analysis of historical boiler records.

Following system start-up and documentation, a 1-year performance test will be made to measure all aspects of LIMB performance. The overall objective of the performance tests is to demonstrate the program goals in conjunction with continuous operation of the LIMB system. Briefly stated, these goals are: (1) significantly reduce SO_x and NO_x emissions, (2) avoid negative impacts on reliability, operability, and steam production, and (3) resolve problems such as increased fouling potential and increased particulate collection and handling problems in a cost-effective manner. Demonstration of each of these goals will require a variety of measurements. For ease of discussion, these measurements are described for the 1-year performance tests only; similar measurements will be performed during the baseline tests.

Emission Characterization. Measurement of emissions during the 1-year test period will be made to establish long-term emission characteristics of the system. The 1-year test period will include three 30-day test sequences when full emission testing will be conducted with optimum LIMB operating conditions. These measurements will include continuous monitoring of SO_x, NO_x, CO, CO_2, O_2, and hydrocarbons using standard EPA sampling and analysis methods. Manual measurement of particulate mass, composition, and size distribution before and after the electrostatic precipitator (ESP) will also be made at frequent intervals. Other measurements, such as fuel analysis and continuous recording of boiler operating conditions, will be made to enable correlation of emissions with parameters that affect emissions.

Boiler Performance and Reliability. Continuous monitoring and/or documentation of steam production, operating time, and outages will be conducted during the 1-year test to evaluate the effects of sorbent injection on boiler performance and reliability. Slagging and fouling characterisitcs during LIMB operation will be determined in tests collecting and evaluating operating data such as steam temperature and pressure drop, visual inspection of radiant and convective sections, and direct measurement of build-up on steam tubes. The extent of corrosion and erosion will be determined by visual inspection and measurement of tube wall thickness at frequent intervals. Solid deposition on furnace walls and tube surfaces will be sampled and analyzed to further identify and quantify problem areas. In addition, monitoring of flue gas temperatures at several points will be made to characterize the boiler thermal environment.

Boiler Operability. Boiler operability is measured by the maintenance and operating requirements of the system. The measurements collected to determine boiler reliability will be used in conjunction with a log which keeps track of how much additional attention, in terms of both manpower and instrumentation, is necessary when LIMB is in operation. The need for additional manpower will be assessed in the data evaluation phase.

Downstream Impacts. The increased solids-loading and the change in particulate characteristics due to LIMB will impact the ESP. These impacts will be assessed by an analysis of the data collected by particulate methods. In addition, samples of the ash will be analyzed for resistivity, and ESP operating conditions will be recorded.

The final downstream impact to be considered will be the handling and disposal of the collected ash. Factors to be measured to assess the ash disposal impacts include amount of additional ash, chemical content, hazardous potential, and handling properties.

Operating Cost. The 1-year test will also be used to gather the data necessary to calculate the operating costs associated with the LIMB system. The capital costs data will be determined from actual invoices. To allow the costs to be calculated later, the on-site analysis will keep track of:

- Sorbent usage,
- Steam production and power generation,
- Fuel input,
- Electrical charges,
- Maintenance requirements (labor and materials),
- Additional operating labor,
- Precipitator operation,
- Limestone feed system labor and power requirements.

DEMONSTRATION RESULTS

Upon completion of the performance test, a final report will be prepared that will address the overall performance of the system in terms of the goals established for the demonstration project. The report will include an evaluation of the LIMB design and its operational and maintenance features and will address the experience gained during construction, start-up, and year-long demonstration. In addition, potential modifications which would improve the technical and cost characteristics of the system will be identified. Finally, the report will present recommendations and guidelines for the further commercialization and applications of the LIMB process to major classes of boilers for both retrofit and new boiler installations.

Although the LIMB Demonstration report is expected to be the focal point of EPA-generated information on the application of LIMB technology, it will, by no means, be the only available aid in extending LIMB technology to other applications. A body of information is now being generated which will address specific aspects of LIMB design and operation, enable extension of the technology to boiler systems differing in design and operation from the demonstration host site, and aid in prediction of LIMB operation and costs for potential boiler applications. This information will include large data bases on various sorbents and coals, design information on low-NO_x burners and other LIMB components, results of combustion studies under a variety of conditions, results of studies to improve removal and collection of ash, and computer models to predict SO_x removal under a variety of boiler design and sorbent injection conditions, just to mention a few. Assuming a successful demonstration of the LIMB system and the generation of supporting applications data, EPA expects that LIMB will become a viable, low-cost commercial technology by 1990.

UNIT CONVERSION TABLE

To Convert From	To	Multiply By
pounds/hour	kilograms/second	1.259×10^{-4}
cubic feet	cubic meters	2.831×10^{-2}
British thermal units/hour	watts	2.928×10^{-1}
degree Fahrenheit	degree Celsius	(T-32)/18
cubic feet/minute	cubic meters/second	4.719×10^{-4}
pounds/square inch	pascals	6.894×10^{3}
tons/hour	kilograms/second	2.519×10^{-1}
square feet	square meters	9.290×10^{-2}
inch/second	centimeters/second	2.54

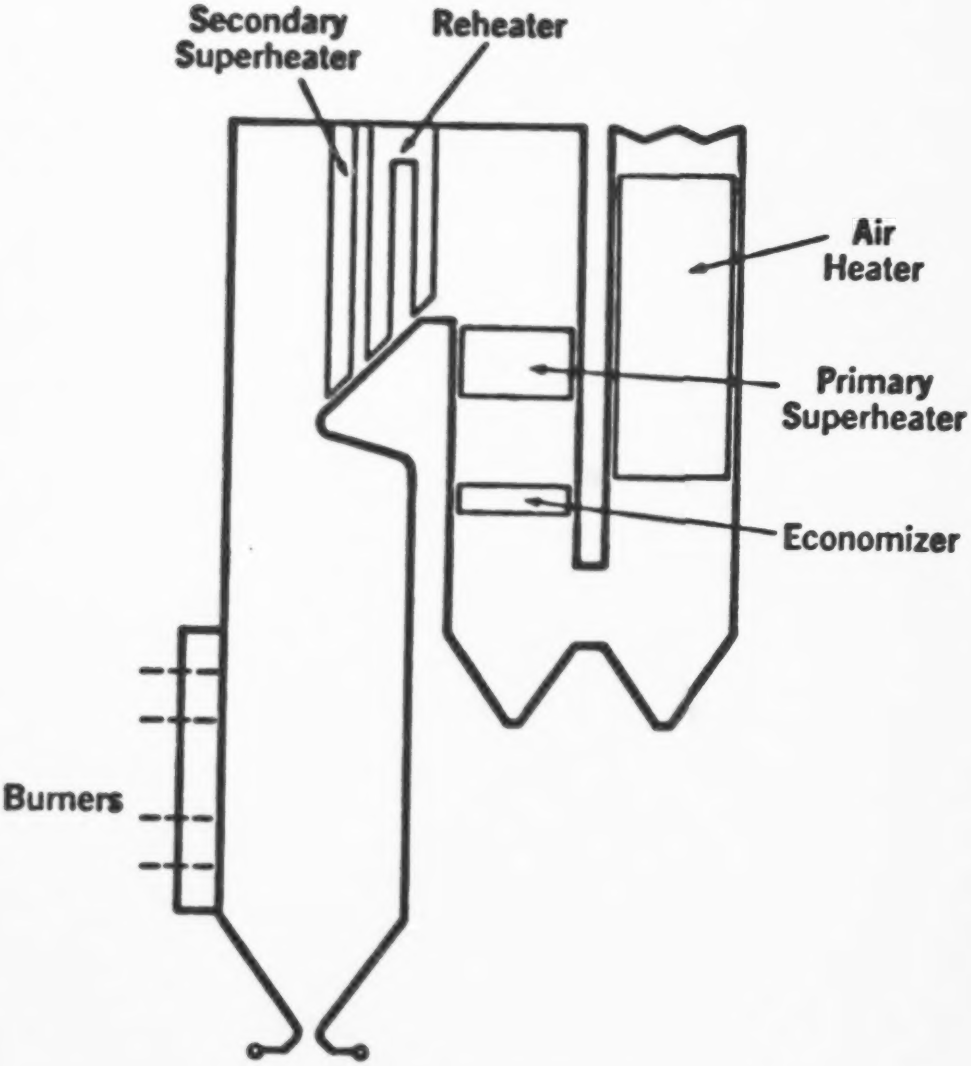
Secondary Superheater
Reheater
Air Heater
Primary Superheater
Economizer
Burners

Figure 1. Boiler Schematic for LIMB Demonstration, Edgewater Station, Unit 4.

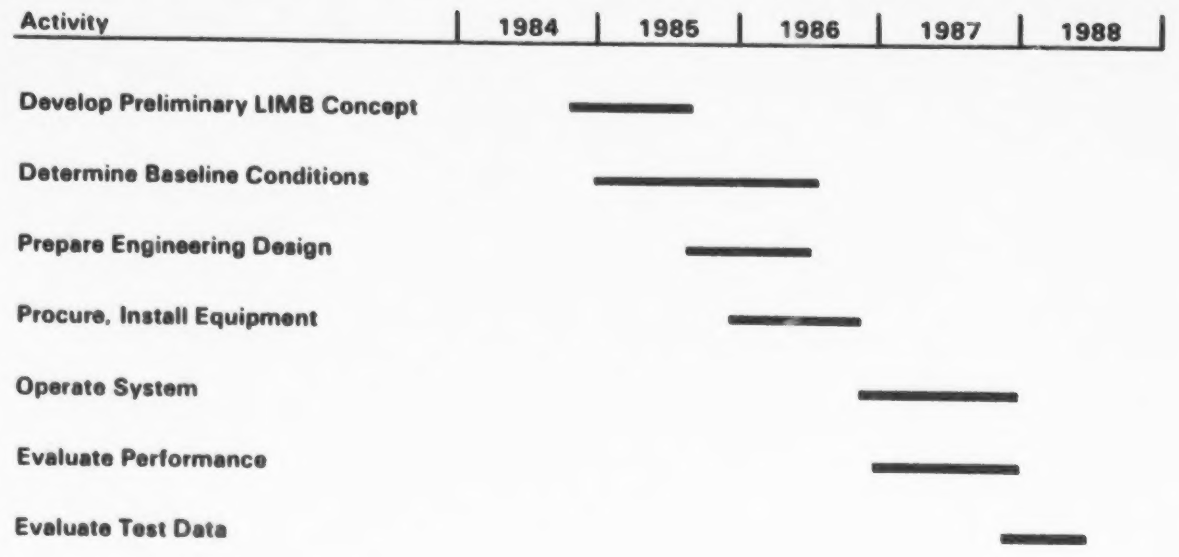

Figure 2. Project Schedule

Table 1

CHARACTERISTICS OF HOST SITE BOILER*

UTILITY - Ohio Edison Company

UNIT - Edgewater No. 4, Lorain, Ohio

RATING - 105 MWe

TYPE - Steam Turbine

INITIAL OPERATION - June 1957

MANUFACTURER - Babcock & Wilcox

BOILER TYPE - Radiant, Wall-Fired

STEAM FLOW - 690,000 lb/hr

DEMONSTRATION FUEL - Ohio Bituminous, 3% or Greater Sulfur

BOILER DESIGN

Furnace Volume - 52,300 ft^3
Heat Release Rate - 9.34×10^8 Btu/hr
Gas Temperatures - Leaving Economizer 605°F
Leaving Air Heater 275°F
Convective Pass Design - Pendant Secondary Superheater and Reheater
Horizontal Primary Superheater and Economizer
Tubular Air Heaters
Sootblowing Capacity - 2 at 1150 CFM, 300 psig each
Coal Mills - 4 mills at 13-14 tons/hr each

PARTICULATE CONTROL

Type - Lodge-Cottrell Electrostatic Precipitator
Installation Date - 1982
Collection Surface - 316,800 ft^2
Design Performance - 518,000 acfm at 280°F at an Efficiency of 99.38%
Design Drift Velocity - 4.2 cm/sec

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* Units most familiar to the reader have been used in this table. A unit conversion table is provided at the end of this paper for convenience.

THE HOMER CITY EXPERIENCE IN DEVELOPING A LIMB PROCESS FOR USE WITH COAL PREPARATION

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ABSTRACT

Pennsylvania Electric and the New York State Electric and Gas Corporation have been experimenting with and further developing a system of Limestone Injection - Multi-Stage Burner (LIMB) that can supplement an existing coal cleaning application to bring their Homer City #3 unit into compliance with EPA's 1971 New Source Performance Standard. Two series of limestone injection tests have been carried out during short runs on the full-scale unit with encouraging results. A series of small scale combustion tests is now being done by selected contractors to lead to the design of a flexible boiler LIMB retrofit. This flexible system will be operated while varying the parameters of injection location, furnace load, firing mode, and limestone type during a four-month test series planned for late-1985. The objectives for the Homer City retrofit are 25 percent SO_2 removal from flue gas containing 1.6 lbs $SO_2/10^6$ BTU using a calcium/sulfur ratio of 1.0 or less. This report presents the results of the Owners' tests to date and their plans for further LIMB development specific to Unit #3.

INTRODUCTION

The Homer City Power Complex is a mine-mouth power plant with three coal-fired boilers. This facility began commercial operation in 1969 with two 600 MW units (Units 1 and 2). A 650 MW boiler (Unit 3) was put into commercial operation in December, 1977. The power station obtains approximately 60 percent of its coal from two dedicated mines at the plant site. The remaining coal is purchased from other mines within 30 miles of the power station.

Units 1 and 2 must comply with an SO_2 emission limit of 3.7 lbs/10^6 BTU, as prescribed by the Pennsylvania Department of Environmental Resources (PaDER). Unit 3 must comply with Federal New Source Performance Standards (NSPS) which limit SO_2 emissions to 1.2 lbs/10^6 BTU.

The owners of the Homer City Power Complex, Pennsylvania Electric Company and The New York State Electric and Gas Corporation, initially considered two different strategies for complying with these emission regulations. The first involved using cleaned coal in Units 1 and 2 and installing a flue gas desulfurization system (FGD) on Unit 3. The second strategy, called the Multi-Stream Coal Cleaning System (MCCS), involved the construction and operation of a coal preparation plant to produce compliance coal capable of meeting both emission regulations at the power complex. An analysis of these strategies indicated that the MCCS would produce substantial operating, maintenance, effluent disposal, and boiler operating cost savings when compared with installation of an FGD system on Unit 3. The MCCS was therefore selected by the owners as the best technology for complying with SO_2 emission regulations at the power station.

The complex MCCS began operation in 1977 but has not been able to clean coal to the conditions specified in the plant design. An extensive test and evaluation program designed to identify and correct the causes of plant operating problems continues. While progress has been made in cleaning sized coal from the Helen and Helvetia on-site coal reserves, current operation dictates that a quality "plateau" at 1.5 to 1.6 lbs SO_2 per million BTU has been reached. Further coal cleaning modifications to reach the 1.2 pound limit have been proposed and are currently being tested by partial incorporation in the plant circuits, but the cost and feasibility of these remedies is not fully known yet.

A LIMESTONE INJECTION SUPPLEMENT

Limestone injection was one of a number of supplementary SO_2 control technologies investigated for use with coal cleaning in the mid-1970's. A full scale test of limestone injection with coal was tried on a 40 MWe unit at Penelec's Front Street Station in 1977. West Virginia University had some bench scale tests of a process that they called "Sulfurtaine" to fix SO_2 in combustion fly ash. While their pilot-scale unit worked very well with the system, Penelec's Front Street unit showed no measurable reduction in SO_2 despite a tremendous increase in particulate emissions during the test.

After that discouraging show, the process was dormant in both Penelec and NYSE&G until it resurfaced with the qualifier of low temperature, low NO_x staged combustion in 1981. The limestone injection process, now the Limestone Injection - Multi-Stage Burner (LIMB) process, emerged once again for Homer City Unit 3 compliance when a state-imposed consent order was about to expire with no practical system for emission reduction at hand. The LIMB system was quickly dusted off and plans for a short-term, full scale trial on Unit #3 with the best available cleaned coal were made.

THE 1982 LIMB TEST

During an annual outage period on Unit #3, seven hundred and fifty tons of high calcium limestone, with a size consist of approximately 1-inch x 1/2- inch, was purchased from M&M Lime Company, R. D. 1, Worthington, Pennsylvania, and stockpiled in the area just adjacent to the coal reclaim hopper. Approximately 550 tons of this material was put into the reclaim hopper and directed to the previously emptied "A" pulverizer storage bunker.

Deep cleaned coal from the low gravity side of the Homer City Coal Cleaning Plant was stockpiled in the clean coal silos for a period of three weeks, and then fed to the specially emptied mill bunkers "B" through "F." The output coal sampled during this stocking operation had a quality to produce an emission level of 1.34 lbs $SO_2/10^6$ BTU.

Several days of delay in the start-up of Unit #3 after its two-week scheduled outage and a last minute forced outage on the "F" pulverizer preceded the limestone test. The original plan was to operate one pulverizer with a limestone feed while carrying full load with the remaining five coal mills.

Testing began with injection of limestone from the "A" mill and clean coal from mills "B" through "E." The "F" mill was inoperable for this phase of the test, resulting in a reduced load for the unit. The initial tonnage was approximately 8.2 TPH. This small volumetric flow may have contributed to feeder problems which resulted in the feeder stopping several times, but it was successfully restarted after each motor overload trip. In order to avoid these feeding problems, the rate was increased to 13.7 TPH until 11:00 PM; at which time the "A" mill was taken out of service until the following morning to conserve limestone.

The following day, limestone was injected at an increased feed rate of 16.4 TPH. The "F" mill had been restored to service and the unit was operating at a 640 MW load. Four hours after reintroducing limestone, the "D" mill, with burners located directly opposite "A," was removed from service, reducing the unit load to 540 MW (gross). This was the same load obtained when the "F" mill was not operable the previous day. Approximately four hours after removing the "D" mill, it was restored to service, increasing the unit to full load at 640 MW. In conjunction with this change, the limestone injection rate was increased to 24.6 TPH and continued until 5:50 AM the third day, at which time all of the limestone supply had been exhausted (see Table I).

SO_2 concentration in the flue gas was monitored continuously before and during injection of the limestone. Limestone samples were collected every three hours from a coal pipe sampler, and analyzed according to procedures defined for calcium content and size distribution. Coal samples were also taken every three hours and analyzed for moisture, ash, sulfur, BTU, and particle size. Samples of dust leaving the air heater were collected by high volume samplers and analyzed for lime reactivity and sulfur content.

For analysis purposes, this test was separated into five test periods with distinct operating variables to distinguish each of them. The average SO_2 removal results for these test periods are shown in Table I. The overall test results concerning SO_2 removal are plotted in Figure 1.

Summarizing the results of this first full-scale, short duration test series:

- SO_2 removal rates were measured by comparing the sulfur level in the as-fired coal (sampled hourly) to the hour-long wet train gas samples. During limestone injection, these removal rates ranged between 20 and 40 percent.

- The removal rates seemed to be more dependent on the firing rate or firing pattern than on the amount of limestone injected between 1 and 3 stoichiometric.

- There did not appear to be any increase in ash deposition caused by limestone injection.

- The secondary, or large, air preheaters experienced an abnormal increase in pressure differential across the elements during this test.

- The electrostatic precipitator performance deteriorated during the injection series. Monitored opacity increased from six percent before injection to 12 or 15 percent during the two stoichiometric runs. In the three stoichiometric run, the opacity approached the 20 percent regulated limit as the test ended.

- There was a perceptible hydration reaction in the fly ash that was generated by this test series. The "water stabilized" and piled ash was noticeably warm, with steam emerging to produce noticeable heaving in the freshly compacted material.

The most interesting result, as far as our respective company managements were concerned, was the Unit #3 had been well within SO_2 compliance during a considerable portion of the test period. A formal Research and Development effort was initiated to further improve the process specific to Unit #3, and it became a viable option in a second Consent Decree that was executed between PaDER and the Owners.

THE 1983 LIMB TEST

A second full-scale, short-term trial was set up on Unit #3 for March of 1983. After receiving technical input from EPA, EPRI, consultants, and others with some LIMB experience, we decided to try injection with coal supplying the two top rows of burners. The test was set up similar to the 1982 trial, except that the unit was about to begin a scheduled maintenance outage period. During the 1982 test, the unit was returning to service from a scheduled outage.

Limestone from the same supplier and coal were pre-mixed to target a stoichiometry of two, and the mix was put into empty coal bunkers of the "A" and "D" pulverizers. Specially produced cleaning plant coal was stockpiled to be used in the other pulverizers in the course of this test. When these pulverizers were placed in service, the test period began. We quickly noticed that the removal rates were not nearly equivalent to those of the earlier test, and that the coal quality was greatly affected by residual coal in the bunkers feeding the other pulverizers. Results of this trial prompted us to try restructuring the test part way through. The remaining limestone was reserved to be fed into the "A" and "D" bunkers after all of the coal/limestone mixture was exhausted. This constituted a second test period within the overall trail.

The results of this second full-scale trial were:

- SO_2 removal was always less than 15 percent when a 1.5 stoichiometric mixture of coal and limestone were fired in the top rows of burners. Both front and rear wall burner rows were used in this test. (Figure 2)

- SO_2 removal ranged between 15 and 20 percent when limestone alone (with considerable coal contamination) was fired.

- The secondary air preheater pressure drop increased perceptibly during the test period; although they had been badly fouled before the test.

- The electrostatic precipitator performance degraded as the amount of limestone feed increased. Opacity was four to eight percent before the test, and increased to 15 percent during the coal/limestone mix trial. When contaminated limestone was fed at two times stoichiometric, the opacity went to 24 percent.

- The ash hydration reaction was noted again.

- No increase in slagging was observed.

AIR PREHEATER EXAMINATION

In the course of the 1983 outage, one major project was to replace the hot and intermediate temperature baskets of the secondary air preheaters. The low temperature elements had been replaced previously, and were found to be clear of deposits after water washing. The hot and intermediate sections were both badly obstructed and badly deteriorated. A program of sampling, destructive basket examination, and deposit analysis was initiated immediately at the beginning of the outage.

Some conclusions reached during this test series were:

- Dilute sulfuric acid, formed when water from the air heater steam blower combined with the sulfur trioxide in the gas, was the primary cause of the air heater fouling. All of the plates had a 0.5 to 1 mm rough layer that bloomed away from the surface and partially blocked the gas passages.
- Fly ash particles readily adhered to the rough layer causing 30-40 percent of the examined plates to have a loose deposit blocking the available air passages. These deposits ranged in length from a few inches to the entire length of the basket.
- All of the deposits originated at areas of severe corrosion near the "cold" end and built up toward the gas inlet. These were easily removed with high-pressure washing; however, low-pressure washing formed a fly ash sludge that promoted additional corrosion.
- The limestone injection tests complicated the problem by depositing calcium oxide and calcium sulfate-rich fly ash on the existing deposits. When exposed to moisture - possibly from the steam-blower or washing - these deposits hardened to cap existing deposits.
- Additional fly ash loading during the test put an even larger burden on the open air heater passages.

While limestone injection was a factor in the air heater fouling, the blockage was due primarily to corrosion of the basket fill material, steam blower operations, and method of cleaning during unit outages.

MODELING STUDIES

After the 1983 test, a program to try and optimize injection locations for Unit #3 using modeling, temperature profiling, and furnace model testing was begun. A number of prospective contractors were requested to provide a series of tests that could meet the following objectives and be specific to Unit #3:

- Optimize the injection process by selecting an injection location that minimizes the amount of injection needed for a 25 percent SO_2 removal.
- Evaluates the effects of limestone injection on boiler operation.

- Evaluates the impact of coal quality (sulfur and ash levels) in SO_2 removal efficiency.
- Provide a preliminary design for a limestone injection retrofit on Unit #3.

A technical evaluation of the proposals received resulted in selection of two contractors, Babcock & Wilcox and Research-Cottrell, to perform work in parallel. Each one has had a history of work in LIMB development, and each proposed a different approach to achieve the set objectives. B&W proposed to do furnace testing on a small scale model with an array of multi-stage burners, while Research-Cottrell proposed to do furnace tests on one nearly full-scale burner operating alone. Both organizations are doing gas flow modeling studies and both will produce a recommendation for injection locations. Research-Cottrell is also studying the problem of ESP operation with low resistivity fly ash.

1985 PROPOSED TESTS

The research and development group has proposed to the Homer City Owners that a temporary system for limestone injection is operated for a four-month period on Unit #3. The injection locations will be those proposed by both B&W and R-C. The R&D group has also recommended that the Owners modify the top rows of burners on both front and rear walls to reduce the flame temperatures in those rows. Other injection locations will also be considered.

During the four-month trial, Unit #3 will be operated for weekly test periods with one discrete set of limestone injection variables fixed; i.e., injection location, firing configuration, limestone type, and coal type. By analyzing the results of these individual runs, the R&D group hopes to find a mode of limestone injection that produces the best calcium utilization with a 25 percent SO_2 removal rate. A 25 percent removal was fixed because Homer City's coal cleaning plant is currently able to produce coal containing less than 1.6 lbs SO_2/million BTUs, and a currently-running program of improvements will certainly improve that operation somewhat. During these test runs, separate experiments will also be structured to determine limestone effects on the convection tubes, air preheaters, ESP, and ash disposal equipment. Successful conclusion of these trials will provide design information that can be used for a permanent installation and modifications to the auxiliary equipment.

Under the terms of the Owners' Consent Decree with the PaDER, the unit must be operating in full emission compliance with limestone injection by December 30, 1988. This research program is structured to meet that compliance schedule. (Table II)

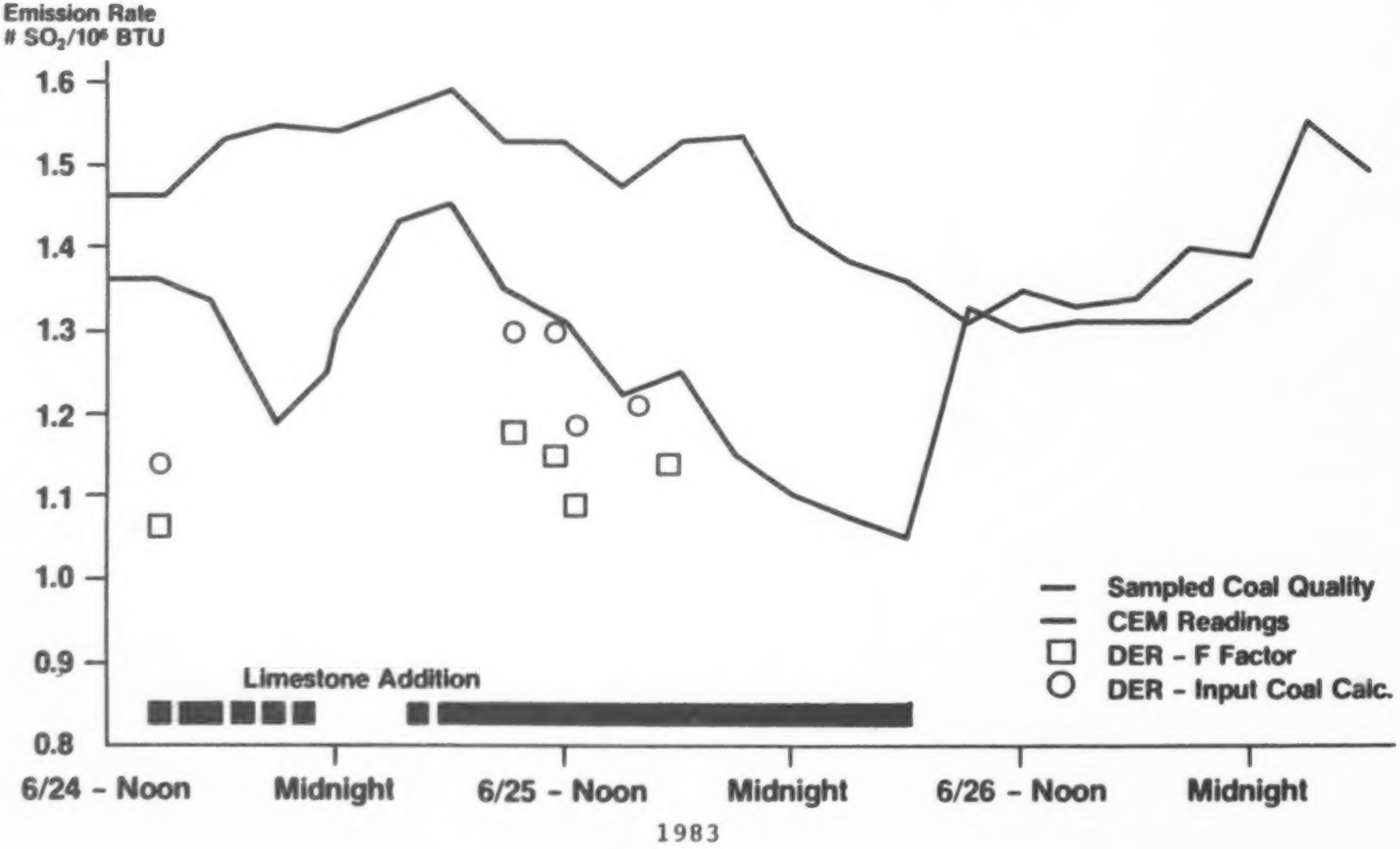
LIMB'S ROLE

The Homer City Owners currently have a number of parallel research and technology improvement programs in process, each with the intent of bringing Homer City #3 into compliance at a reasonable cost. Limestone injection appears to be highly competitive with these other compliance scenarios because it promises increased flexibility in purchasing, processing, and blending coal for the unit at a reasonable installation cost. We also note that it could be the only low cost candidate that can maintain its full removal rate in accord with the current three-hour emission averaging that is used to determine compliance.

The limestone injection research program at Homer City is still dependent upon the results of a number of other events that influence the unit's legal status. Near term developments will determine how far the injection technology for Unit #3 will be pursued.

CONCLUSION

The Homer City Owners view limestone injection as a feasible, low cost process to supplement coal cleaning on Unit #3 for SO_2 emission compliance. Preliminary tests have indicated that the process is workable and that boiler equipment can be modified to operate with limestone injection. Future work to optimize the process, its reagents, and to promote further downstream SO_2 capture can further enhance a workable system that will soon be developed for Unit #3.



HOMER CITY #3 UNIT
INPUT COAL QUALITY & MEASURED EMISSIONS
VS. TIME

FIGURE 1

FIGURE 2
LIMESTONE INJECTION TEST II
EMISSION RATE
SO$_2$/10^6 BTU

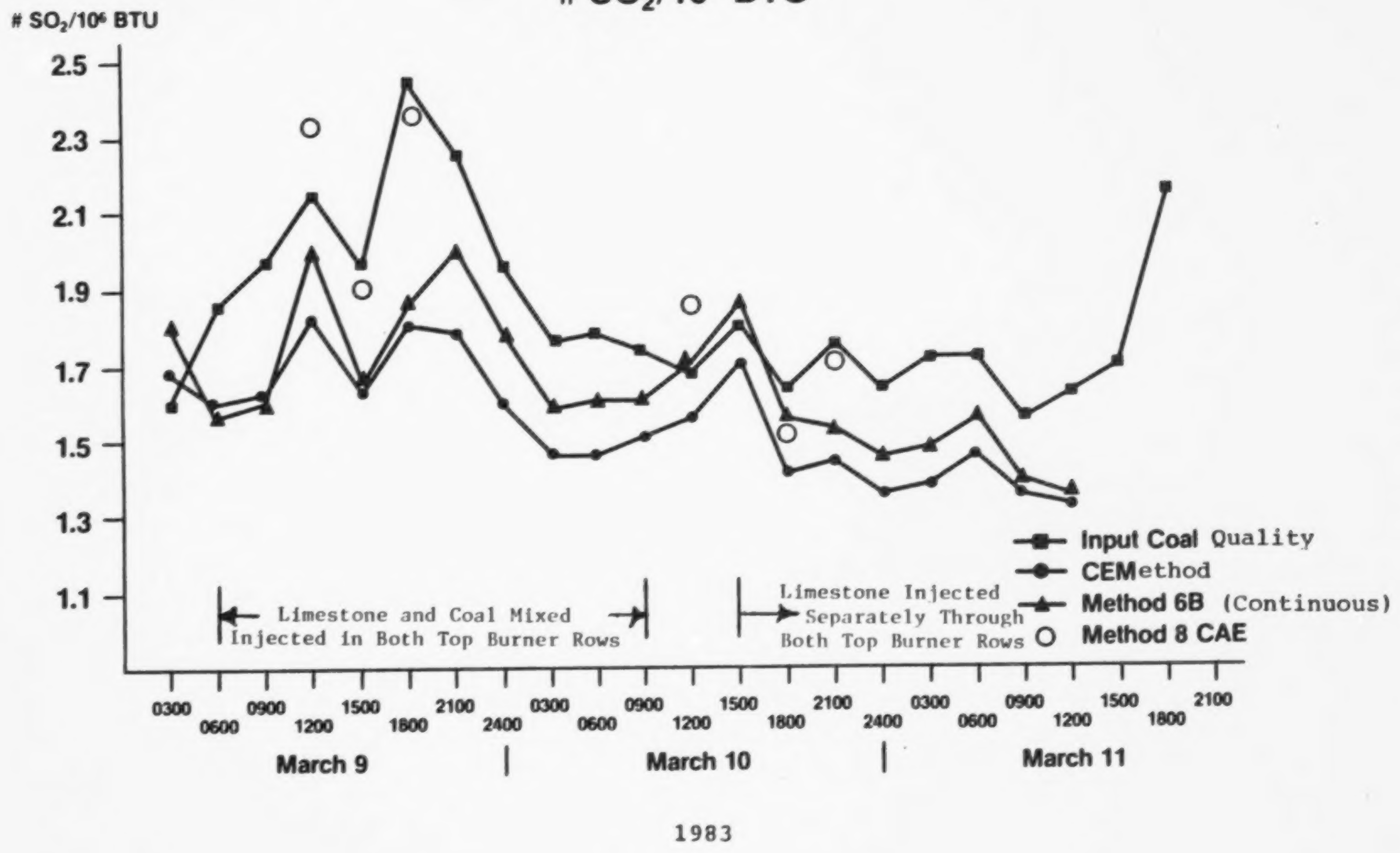


Table I

HOMER CITY STATION - UNIT #3
DRY LIMESTONE INJECTION TEST RESULTS

Gross Generation (MW)	Boiler Operation	Limestone Injection Rate (Tons/Hr)	Input Coal Quality (# $SO_2/10^6$ BTU)	Emission Rate (# $SO_2/10^6$ BTU)		% Emission Reduction @ Input Coal
				F Factor	Calculated* @ Input Coal	
540	"F" Mill Off	13.7	1.53	1.171	1.031	30.0
640	Full Load	16.4	1.53	1.260	1.233	23.8
640	Full Load	16.4	1.53	1.249	1.187	24.7
540	"D" Mill Off	16.4	1.47	1.137	1.150	26.1
640	Full Load	24.6	1.53	1.194	1.209	25.7

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*DER preferred method. F Factor used as backup.

Table II

DEVELOPMENT SCHEDULE - LIMESTONE INJECTION FOR HOMER CITY #3

To November 30, 1984 -- Pilot-scale tests designed to optimize SO_2 capture in Homer City #3.

February 1, 1985 -- Begin installation of a partial LIMB/LI conversion to quantify removal efficiency and long-term operating effects.

August 1, 1985 -- Unit outage for installation of injection ports.

September 1, 1985 -- Begin testing the partial conversion.

January 1, 1986 -- Begin detailed evaluation of partial conversion.

April 1, 1986 -- Report due on partial conversion.

May 1, 1986 -- Begin detailed engineering on a full-scale conversion with auxiliaries for Unit #3.

March 1, 1988 -- Start-up full-scale Unit #3 conversion.

June 1, 1988 -- Begin performance tests - Unit #3 LIMB conversion.

December 31, 1988 -- Compliance with consent decree.

NO_X/SO_2 CONTROL EXPERIENCE AT SASKATCHEWAN CORPORATION'S BOUNDARY DAM G.S. -- UNIT #6

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INTRODUCTION

Fossil electric power generation in Canada uses coal as its primary fuel source and with its use public concern has escalated about the control of SO_2 and NO_x emissions due to their environmental impacts. Western Canadian coals typically contain .3% - 1% sulphur, whereas Eastern Canadian coals typically have sulphur contents of 2% - 5%. Consequently, SO_2 emission control philosophies should be tailored to meet the severity of the specific problem. Similarly with NO_x, different coals and different firing conditions will dictate the necessity of different systems for NO_x control. The current Canadian federal emission guidelines for both SO_2 and NO_x emission is 0.6 lb/10^6 Btu. (258 ng/J).

Presented in this paper are test results of C-E Canada's Modified Combustion Technique, which reduces SO_2 and NO_x emissions. The work was done in 1983 and 1984 at Saskatchewan Power's Boundary Dam Generating Station. The system includes overfire air and Low NO_x Concentric Firing (LNCFS) with limestone injection for the control of both SO_2 and NO_x emissions. This paper discusses operation, test results, economic feasibility and gives a programme for ongoing test work.

The test work was carried out with a Saskatechwan lignite containing .3% -.5% sulphur and a heating value of 6600 Btu/lb. (15300 kJ/Kg)

It is felt that this demonstration in a unit of 300 MW in an actual operating environment provided substantial benefits in the development of this promising new technology.

STEAM GENERATOR DESCRIPTION & MODIFICATIONS

The test unit for this project was Saskatchewan Power Corporation's Boundary Dam Unit #6 - a Combustion Engineering natural circulation tangentially fired unit with a divided furnace. (Figure 1). The unit was constructed and commissioned in 1978 and is rated at 300 MW output. The unit performance data is indicated in Table 1 with a typical analysis of the lignite coal fired in Table 2. This coal has a low sulphur content typical of many Western Canadian coals and has a high inherent calcium to sulphur ratio. The heat release rate per plan area in the furnace is typical of lignite fired units (1.46×10^6 Btu/hr ft^2) (4600 KW/m^2) and therefore would be relatively low compared with a furnace designed to fire bituminous coal.

Prior to modification, the firing system was a conventional divided furnace with a C-E Tangential Firing System consisting of eight (8) windboxes, each containing a series of coal and air compartments. With the C-E system one pulverizer feeds one elevation of burners. The arrangement of the windboxes is depicted in Figure 2. There are five (5) elevations of coal nozzles with adjacent auxiliary air ports and an uppermost integral overfire air compartment.

In the spring of 1983 modifications were performed to the windboxes of one furnace to convert it to a C-E Low NO_x Concentric Firing System (LNCFS) for the admission of auxiliary air. The arrangement of these offsets and nozzles is shown in Figures 3 and 4. For the test, concentric firing air nozzles were installed having the capability of tilting horizontally as well as vertically (typically both fuel and air nozzles have the capability of tilting only vertically). The distribution and control of primary air, auxiliary air, fuel air and overfire air in both sides of the divided furnace were modified.

NO_x AND SO_2 FORMATION

The two major pollutants resulting from thermal power generation are NO_x and SO_2. NO_x, which is a collective reference representing both NO and NO_2, will form in and around the high temperature regions of the flame as a consequence of the combustion process. The formation of nitrogen oxides is derived from two sources, nitrogen contained within the combustion air and that contained in the fuel. NO_x formed from nitrogen contained within the fuel, termed fuel NO_x, is dependent on oxygen and nitrogen in the fuel which varies with the rank of coal. The NO_x formed from fuel nitrogen can best be controlled by limiting the oxygen concentration in the primary combustion region, fuel NO_x formation is relatively insensitive to temperature. NO_x formed from the fixation of atmospheric nitrogen, termed thermal NO_x, is very much affected by flame temperature and to a lesser degree by available oxygen. Overfire air and LNCFS employ the principles of reducing flame temperatures while removing available oxygen and nitrogen from the primary flame zone to reduce the NO_x emission levels.

SO_2 and SO_3 are formed from the combustion of sulphur contained within the coal. However, the amount of SO_3 usually accounts for less than 1% of the total sulphur oxide emission. SO_2 discharged to the atmosphere contributes to 'acid rain' formation. "Direct furnace sorbent injection" refers to a sorbent which is pulverized in much the same manner as coal and then injected directly into the furnace. In this specific situation limestone was used as the added sorbent. It was inter-mixed with the coal at the feeder level after which it underwent pulverization and was theninjected into either of the bottom two coal elevations.

The inorganic material in many coals contains calcium and other basic compounds which are available to react with the SO_2. This was the case with the lignite tested at Saskatchewan, at least half of the calcium reported in the test results originated from the ash.

Upon entering the furnace the limestone undergoes calcination where CO_2 is freed in a manner depending upon the type of limestone and initial heating rate leaving CaO. Under suitable furnace conditions, solid CaO will then inter-mix with the gaseous SO_2 to create a reaction in which solid calcium sulphate ($CaSO_4$) is formed. This solid product can then be removed by a precipitator and disposed of. These reactions are dependent upon temperature, and for optimum capture rates the sorbent (i.e. limestone) should be injected away from the higher temperature portions of the flame. At very high temperatures limestone particles will sinter and lose their porosity, thus becoming chemically unreactive. The capture rate is also very dependant on both the degree of mixing and the residence time of the limestone in the furnace.

The reduction of SO_2 and NO_x is complementary when sorbent injection philosophy is applied in combination with the low NO_x burner technology due to the inherent lower combustion temperatures, which provide appropriate conditions for both NO_x reduction and SO_2 capture.

OPERATION

An important part of the Boundary Dam Station test programme was to demonstrate that the Modified Combustion Techniques, either in combination with limestone injection or without it, could be operated successfully by the plant staff and control systems and that there would be no significant adverse effect on unit reliability, efficiency or slagging.

Since the test started in May 1983 the unit has operated successfully with some form of the Modified Combustion Technique. Continuous limestone injection for SO_2 control has only been used during the test periods. The control room operators are not aware of any differences in operation with the modified combustion technique. To take full advantage of the system, a more complex air distribution control system would be required to control: the oxygen in the primary burner region, the desired overfire air amount, the desired auxiliary to fuel air ratio, and the air velocity or windbox to furnace differential pressure. During the tests these ratios were manually set at MCR and the dampers left in that position during operation.

The C-E Low NO_x Concentric Firing System incorporates auxiliary air nozzles that offset a portion of combustion air outside of the primary firing circle, hence, the name concentric firing. Introducing auxiliary air outside of the primary combustion zone results in a significant portion of the nitrogen and oxygen contained in the auxiliary air being removed from the high temperature primary flame region, and also results in the lowering of flame temperature in this region. The auxiliary air which comprises a significant amount of the total combustion air is directed along the walls. Tests have shown that an oxygen rich layer is formed around the complete perimeter of the furnace. This rich oxygen zone is felt to be responsible for the reduction of slagging in the burner region of the furnace due to maintaining the ash constituents (the ash fusion temperatures are higher in an oxidizing atmosphere than in a reducing atmosphere) in an oxidizing atmosphere and by providing an air screen through which the ash particles have to pass in order to impinge on the furnace walls. At the same time this produces a reducing atmosphere at the centre of the furnace which aids in overall NO_x control.

Figure 5 shows that the furnace ash deposition was evaluated as being less severe with the LNCFS firing compared to the normal tangential firing. An overall average assessment of furnace deposits indicates a reduction in furnace slagging of approximately 20% in the LNCFS furnace, with the major reduction in slagging being nearer the corners of the unit. This was felt to result from relatively low concentric air velocities compared with normal design velocities, because only a portion of the burner compartments were altered.

During the test period the rate of fouling in the superheater region was monitored using ash deposition probes. Due to the limestone injection and the lower rate of ash deposition in the furnace there would be a slightly higher ash loading to the superheater. In the case of the Boundary Dam test, the increased ash loading was not of major significance due to the fact that the bulk of the calcium present was inherent in the coal ash. It was possible to keep the superheaters and the reheaters clean throughout the test period by normal sootblowing cycles.

The addition of limestone to the furnace results in a modified ash composition within the furnace and superheater regions. Depending upon the ash composition, the addition of calcium may either increase or decrease the average ash fusion temperatures. In the case of the Saskatchewan lignite with the relatively high sodium content, the addition of limestone was normally beneficial in increasing the ash fusion temperatures thereby reducing the slagging and fouling problems in both the furnace and superheater. It is important to realize that with other fuels the addition of limestone might substantially depress the ash fusion temperatures and cause increased rates of slagging and fouling, even in boiler regions not normally subjected to deposits.

The carbon in the fly ash was measured in many of the tests. However it was not possible to correlate the carbon loss with any of the operating parameters such as furnace oxygen level, percent overfire air or ratio of auxiliary to fuel air. During the test period the pulverized fuel sizing was relatively coarse with 50% to 60% through a 200 mesh screen, and the carbon in the fly ash varied from .5 to 1.5% with 1% carbon in the fly ash representing an efficiency loss below .2%. Previous tests have indicated that under modified firing conditions and particularly low O_2, (used in order to reduce NO_x levels) that the carbon in the fly ash had increased. Using lignite with a fineness of 65% through 200 mesh, carbon in the ash increased from 0.1% at normal excess air levels and operating conditions, to 1% using 1% O_2 levels and maximum overfire air operation. In a unit designed initially for Modified Combustion Techniques the coal fineness and degree of turbulence would be increased slightly in order to maintain the desired heat loss due to unburnt combustible matter and the overall unit efficiency.

The unit operated reliably and without serious problems throughout the test program, and for over a year since the conversion, with the operation continuing to be similar to that with conventional firing techniques. Since the installation of the LNCFS buckets, the fuel content has varied over its normal range including variations in sulphur, sodium, moisture and calcium contents without demonstrating any abnormal operating conditions.

TEST RESULTS

The major objectives of the emissions research portions of the test were to investigate the following:

1) The effect of combustion modifications such as overfire air and LNCFS on NO_x emission level;

2) The effects of combustion modifications on SO_2 capture by sorbents inherent to the coal ash;

3) The additional capture rates achievable through the use of injected sorbents;

4) The effects of combustion modifications and limestone injection on ash deposition within the furnace.

Prior to converting one of the furnaces to concentric firing, some baseline test work was done in 1982. Following the installation of the concentric firing air nozzles three periods of tests were carried out at

Saskatchewan Power Corporation's Boundary Dam G.S. In all, over 100 test configurations were used and the variables included primary air flow, auxiliary air flow, fuel air flow, overfire air flow, excess air level, LNCFS and nozzle deflection angle.

The first series of post modification tests were conducted in June and July of 1983 to determine the effects of the LNCFS system on NO_x formation. Most of these tests were conducted with the unit running at full load with the offset angle of the LNCFS nozzles at maximum (25°). Figure 6 shows the effect of varying the offset angles of the LNCFS nozzles and the amount of overfire air. At full load, the lowest NO_x emission level measured during the first post modification test period varied between 167 and 195 ppm which is a 57% to 63% reduction from the baseline during normal operating conditions. This same range of NO_x emission levels and reduction was then demonstrated during the sorbent injection testing.

The effect of limestone injection on SO_2 reduction at various calcium to sulphur ratios was also investigated. The inherent calcium to sulphur ratio of the coal varied between 1.5 to 2.5 and injected amounts increased this ratio up to 3.8. The capture rates were influenced by several factors and increased as the concentration of SO_2 formed increased, and as the calcium to sulphur ratio increased.

Figure 7 is based on a capture rate from a theoretical sulphur content in the coal as determined by our laboratory analysis. Another curve is shown using an extrapolation based on a different coal sulphur content which, as noted previously, results in higher captures based on the greater SO_2 formed.

For the Boundary Dam tests with .34% sulphur, the SO_2 removal with a calcium/sulphur ratio of approximately 2.5 was 42%; extrapolating this to a typical .5% sulphur fuel would give a capture in the order of 50%.

In November 1983 a second series of post modification tests was conducted. Its purpose was twofold: a verification of previous results, and more detailed work with regard to sorbent injection and the SO_2 emission study. The results of these tests essentially verified the previous results.

PRELIMINARY ECONOMIC EVALUATION

Initially the C-E Canada Modified Combustion Technique for sorbent injection was targeted at low sulphur sub-bituminous and lignite fuels. It is felt that the system would be economically attractive for these fuels because of their relatively low sulphur content (in Canada) and because they contain a significant amount of alkaline materials in the ash. In these cases, the capital cost of an installation is going to be low relative to other alternatives such as dry and wet scrubbing, the operating costs (excluding sorbent utilization) will be low compared to alternative technologies, and the cost of limestone would be similar to alternative technologies for the same removal efficiencies (40% to 60%). The economic studies and research to date indicate that this conclusion is correct, and preliminary economic studies by C-E Canada indicate that this system may be competitive for fuels containing sulphur content in the region of 2%.

The major factors affecting the economic evaluation are:

1) The fuel analysis, particularly the sulphur and inherent calcium sulphur content;

2) The type of firing system utilized;

3) The furnace heat release rate (temperature profile);

4) The cost and reactivity of limestone sorbent;

5) The percentage sulphur capture required to meet emission guidelines.

On retrofit installations the suitability of existing equipment to operating under the new conditions is also a significant factor. This includes the performance of the electrostatic precipitator or bag filter, the capacity of the ash removal systems, and the sootblower coverage. In addition, the retrofit installation must have suitable real estate for the addition of a limestone handling and pulverization system, and sufficient space to fit the limestone injection system to the furnace.

A C-E Inc. study undertaken for EPRI on the feasibility of limestone injection for SO_2 control on a 500 MW unit demonstrated that the system could be economic for coals containing sulphur contents up to 4%. The advantage of the modified combustion technique for limestone injection is the low capital cost. However, in the case of higher sulphur fuels the sorbent cost would tend to be higher than for other types of systems (i.e. flue gas desulphurization). This C-E Inc. study considered the alternative of purchasing lower sulphur fuel. Clearly the economic picture with regards to the Modified Combustion Technique with sorbent injection is enhanced for units burning variable sulphur fuels and for operation at lower load factors, where the lower capital cost may more than compensate for the higher sorbent costs.

The estimated cost of this technology (including limestone pulverization equipment costs) for a new unit handling Western Canadian coal with a sulphur content below 1% will range from approximately \$22/kW to \$15/kW installed, for unit sizes of 150 and 400 MW, respectively. For retrofitting units, (not including the upgrading of the particulate collection equipment) the costs are approximately \$28/kW and \$20/kW installed for unit sizes of 150 and 400 MW, respectively.

It should be noted once again that these capital costs are very much lower than the capital cost of any other comparable SO_2 removal technologies and the added advantage of the C-E Canada Modified Combustion Technique is that it will reduce nitrogen oxide emission levels as well as SO_2.

CONCLUSIONS & FUTURE PLANNING

The C-E Modified Combustion Firing System with direct limestone injection has proven to be an effective and viable method of reducing NO_x and SO_2 emissions that result from burning Saskatchewan lignite. Results derived from three series of tests conducted at Saskatchewan Power have shown that a 50% to 60% reduction in NO_x levels can be achieved compared with conventional tangential firing. The SO_2 emission levels for lignite were reduced on average to 50% of the theoretical levels generated utilizing mainly the inherent alkalai material of the lignite with a calcium to sulphur molar ratio of 2:1 based on a .5% sulphur coal. These tests also demonstrated that direct sorbent injection into the combustion chamber will further reduce SO_2 emissions. The results of these tests showed that this technique can be effectively used to reduce the SO_2 emissions of the tested lignite to meet the present federal guidelines of 0.6 lb/10^6 Btu (258 ng/J).

A significant conclusion of these tests was that the boiler with the modified combustion technique can be successfully operated and controlled by existing plant staff and control systems. It was also determined that the increase in carbon loss due to the firing modifications was insignificant. Slagging in the lower furnace was less severe during tests with the Modified Combustion Technique. Sorbent injection was found to increase the ash shedding rate and unit cleanliness was maintained with routine sootblowing operation.

Additional research work is planned in the near future. Saskatchewan Power and Combustion Engineering Canada are planning the demonstration of an improved combustion system in the near future. This major demonstration would investigate improved burners, location of overfire air, location of limestone injection and sizing of limestone further to tests reported herein.

(Unpresented Paper)

SUCTION PYROMETRY TESTS ON INNOVATIVE FURNACE

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ABSTRACT

Suction pyrometry tests were conducted on the Environmental Protection Agency innovative furnace in the Environmental Research Center to establish the actual gas temperatures at several points in the furnace at specified operating conditions. Gas residence times were calculated using the temperatures established by the suction pyrometry tests and gas compositions measured by the monitors. At the selected firing rate of 47,300 Btu/hr (14 kW) thermal input, gas residence times of approximately 1.5 seconds between the temperatures of 2250 and 1600°F (1232 and 871°C) were calculated.

INTRODUCTION

Northrop Services is responsible for the operation and maintenance of a pilot-scale coal burning furnace owned by the Environmental Protection Agency. The furnace is used to study techniques for limestone injection through a multistaged burner (LIMB). The purpose of the LIMB furnace is to test innovative combustion technologies: specifically, methods to reduce SO_2 emissions from coal-fired burners. The primary SO_2 reduction technique to be tested is the injection of limestone at various points in the furnace and/or burner. From previous laboratory studies, it has been shown that two important furnace parameters that affect SO_2 capture on limestone are: the temperature profile in the furnace and the residence time. This paper presents the results of testing to determine the temperature and residence time of the gases in the LIMB furnace.

The LIMB furnace is versatile in operation in that air and fuel can be injected into the furnace at a number of points. The exact configuration and combustion conditions will be a function of the research objective of each test plan. To estimate the temperature, a baseline configuration was chosen. This condition was to have all the fuel and combustion air mixed at the burner. (Note: A small flow of air is always metered to the gas pilot to prevent heat damage.) The air and fuel combust, and the resulting hot flue products travel through the refractory core of the furnace and then pass through a water-jacketed section--to reduce the temperature and quench any reactions that may be occurring. Extensive temperature measurements were conducted with this furnace configuration employing various excess air rates while burning both propane and coal. After these tests were completed, the effect of adding staging air (or sorbent carrier air) was also investigated.

Measurement of the furnace temperatures and residence times took place in two phases. Figure 1a is a schematic of the LIMB furnace as it was originally designed. Tests conducted on this furnace configuration are referred to as Phase I. Figure 1b is a schematic of the furnace after two new sections were added increasing the furnace length by 36 inches (0.91 m). Tests conducted on the longer furnace are referred to as Phase II. As part of the furnace, Type B thermocouples are permanently located at various distances from the burner (see Figure 1a and b for dimensions). The thermocouples are recessed approximately 1 inch (25.4 mm) back into the refractory and therefore do not come in direct contact with the flue gases. All the thermocouples are wired into one of two selective readouts on the control panel. To measure the true temperature of the gas stream it is necessary to sample at the ports located in the furnace. The following section gives a brief explanation of the theory used in making temperature measurements. See Appendix A for sample calculations.

GAS TEMPERATURE MEASUREMENT THEORY

There are numerous methods and sensors that can be used to measure temperature. In all cases, the temperature sensing element approaches a temperature in equilibrium with the conditions of its environment. A temperature sensor receives heat primarily by convective heat transfer from the hot gases in which it is immersed. However, the sensor is also subject to heat loss or gain by radiation to and from the surrounding surfaces and to a lesser extent by conduction through the instrument itself. Therefore, if the temperature of the surrounding surfaces is higher or lower than that of the gases, the temperature of the sensor will be correspondingly higher or lower than the true temperature of the gases (due to radiation losses or gains).

For testing in the LIMB furnace, the best instrument available for negating radiation losses and therefore measuring the true temperature of gases was determined to be a multiple-shield, high-velocity thermocouple (MHVT) also referred to as a suction pyrometer.(1) Figure 2 illustrates the suction pyrometer used to measure temperature in the LIMB furnace. These devices consist of a pair of small diameter thermocouple wires surrounded by a series of ceramic shields which isolate the thermocouple from the surrounding radiation. A known volume of flue gas is pulled over the shields containing the thermocouple. By inducing a high rate of gas flow over the shields, the transfer of heat due to convection increases while the losses due to radiation are minimized. The small diameter thermocouple wires (approximately 0.25 mm) negate conductive heat losses. Therefore, the temperature of the thermocouple junction may be brought to equilibrium with the true temperature of the gases.

The output of a suction pyrometer increases to an equilibrium maximum, with an increase in gas mass velocity flowing between the outer and inner shields. Figure 3 illustrates this relationship between mass velocity and temperature indicated by a suction pyrometer. It is important when performing suction pyrometer testing to ensure that an adequate mass velocity is maintained. It is recommended that the gas mass velocity between the shields not be less than 15,000 lb/ft^2 hr (1,221 kg/m^{2}s).(1) A curve similar to that illustrated in Figure 3 should be developed for each individual suction pyrometer design. (See Appendix B.) This is accomplished by sampling at a low gas mass velocity (approximately 10 percent of capacity) and recording the corresponding temperature; the gas mass velocity is then increased and a new temperature recorded; and eventually the temperature will reach a plateau (equilibrium). This temperature is the true temperature of the gas stream, and the corresponding gas mass velocity where the temperature levels off is the minimum flow rate that must be pulled for that pyrometer design.(2)

EQUIPMENT AND PROCEDURES

Figure 2 is a schematic of the suction pyrometer used to measure gas temperature in the LIMB furnace. The following is a list of the individual equipment pieces:

1. Outer ceramic shield

    - 1/2-inch (12 mm) inner diameter
    - 3/8-inch (9.5 mm) hole at tip
    - 99% + alumina

2. Inner ceramic sheath

    - 3/8-inch (9.5 mm) outer diameter
    - 1/4-inch (6.4 mm) inner diameter
    - 99% + alumina

3. Ceramic thermocouple wire support

4. Thermocouple wire

    - platinum - 6% rhodium
    - platinum - 30% rhodium
    - each wire 0.01 inch (0.25 mm) diameter

5. Water jacketed stainles steel probe

6. Condensation trap - impinger system

7. Pump

8. Dry gas meter

The following procedures were followed when conducting a suction pyrometer test:

1. The impingers, pump, and dry gas meter were assembled according to the procedures given in EPA Reference Method 5.(3) The first two impingers were charged with approximately 200 ml of water, the 3rd impinger was left dry, and the 4th impinger was loaded about 1/3 full of silica gel.

2. The system was then leak checked from the sample line probe junction, back through the dry gas meter. A leak was any flow greater than 0.02 cfm (9.4 $\mu m^3/s$) with the line plugged.

3. The suction pyrometer was assembled by threading the two thermocouple wires through the holes in the ceramic support, and then welding them together. The support was then placed inside the inner sheath, and the sheath was then put inside the probe. The back-end of the sheath/probe

was sealed with ceramic cement to prevent flue gases from bypassing the sample line. Finally, the outer ceramic shield was placed over the sheath so that the thermocouple junction was 1/4 to 1 inch (6.4 mm to 25 mm) downstream of the hole in the shield.

4. The water and sample lines were then connected to the probe. The Type B thermocouple connector wires were connected from the pyrometer to the panel temperature readout. (Note both panel and pyrometer used the same readout.)

5. Before initial testing, the pyrometer was inserted into the stack along with a Type K thermocouple, to provide a quick check as to the reliability of construction of the pyrometer. A Type K thermocouple was inserted into the double-shielded area of the suction pyrometer; i.e., it replaced Type B. This Type K thermocouple was then inserted into the stack at a port where the temperature is approximately 1300°F (704°C). Next, the suction pyrometer with the Type B thermocouple was placed in the same port. No flow was pulled on either. The pyrometer was accepted as satisfactory if the two temperatures were within ± 5 percent. This was done to verify adequacy of construction of the pyrometer, not as a calibration.

6. The probe was then marked off so that the hole in the shield is at the sample point; i.e., the middle of the stack.

7. The pyrometer was allowed to reach thermal equilibrium without suction, and the static temperature recorded.

8. A temperature versus sampling rate curve was initially developed for this pyrometer configuration at each sampling port. The pump was turned on and adjusted to pull approximately 10, 25, 50, 75, and 100 percent of the maximum sampling rate. At each sampling rate, the equilibrium temperature and exact sampling rate were recorded.

9. From testing it was determined that at least 15,000 lb/ft^2 hr (1,221 kg/m^{2}s) or 2.0 scfm (994 μm^3/s) measured at the dry gas meter must be pulled to reach equilibrium. In subsequent tests, only one sampling flow rate was pulled. This rate is in excess of where the temperature leveled off. This flow rate constitutes 20 to 50 percent of the total flow in the furnace.

RESULTS AND DISCUSSION

Numerous suction pyrometer tests have been conducted at the LIMB furnace. Tests were conducted first to determine the true temperature profile and residence times at a given firing rate and then to determine if/how furnace variables (e.g., burner design, excess air) affect the temperature profile. Also as a result of tests performed, two new sections were added to the furnace. Results of the earlier suction pyrometer tests, with the shorter furnace, are discussed in Phase I, while results of testing the current furnace are given in Phase II.

Phase I Testing

Initial testing was begun using a propane firing rate of 67,500 Btu/hr (19.8 kW), which is equivalent to burning 5.0 lb/hr (0.63 g/s) coal. The stoichiometric ratio (SR) of combustion air to fuel was set at 1.1 (or also referred to as 10 percent excess air). It was originally assumed that firing propane or coal at this rate would produce the desired temperature profile and an adequate residence time to perform limestone injection testing. Results of these suction pyrometer tests, plotting residence time versus measured temperature, are given in Figure 4. Frequent breakage of the ceramic shield and sheath occurred during the early tests. Therefore, the two tests in Figure 4 were performed over a period of days. As can be seen from this figure, the upper temperatures are close to 3000°F (1649°C) and the residence time of the flue gases in the furnace is less than 1.0 second. To reduce the temperature and increase the residence time, lower fuel firing rates were tested.

As noted in the theory section, to ensure that the true temperature of the gas is being measured, curves showing the relationship between pyrometer mass flow rate versus temperature must be developed. For the data in Figure 4, these curves are presented in Appendix B. From these curves it was noted that at least 15,000 lb/ft^2 hr (1,221 kg/m^{2}s) [or 2.0 scfm (900 μm^3/s) measured at the dry gas meter] must be pulled over the thermocouple junction to reach an equilibrium temperature--i.e., the flat portion of the curve. Dependent on the firing rate and stoichiometric ratio (SR) this sample rate can represent 20 to 50 percent of the total volume of flue gases in the furnace. Pulling this large a percentage of the total volume will eventually affect furnace conditions; however, this did not appear to affect the measured gas temperature. First, the sampling time is short, approximately 2.0 to 5.0 minutes at each port. Secondly, before any sampling was performed the furnace was allowed to equilibrate for at least 16 or more hours at the desired conditions. Therefore, it was assumed that upsetting the furnace conditions for that short a period of time would not greatly affect the thermal profile of the system since thermal inertia was so great.

The next firing rate tested was 47,300 Btu/hr (14 kW) which corresponds to burning 3.5 lb/hr (0.44 g/s) coal. This value was chosen because it is the lowest feed rate of propane that can be burned in the furnace while simultaneously injecting limestone at the burner. At lower propane flow rates, combustion conditions in the furnace become very erratic. Figure 5 shows the results of two suction pyrometer tests performed at this lower firing rate. Both tests were performed while burning at an SR of approximately 1.25. However, after the test on 11/8/83, a new section of furnace was added between the fourth port and the water jacketed section. The new furnace section does not have a port, so no suction pyrometer data is available. A thermocouple, recessed 1 inch (25.4 mm) into the refractory, gave a temperature readout of approximately 750°F (399°C). This temperature is at least 200 to 400°F (93 to 204°C) cooler than the gases inside the section. Temperature profiles and residence times at this lower firing rate were now very close to an acceptable range. A summary of the data for these tests is given in Table 1.

Phase II

Radial Burner. To improve the temperature/residence time of the flue gases in the furnace, two new sections of furnace were added. In addition, five new sampling ports and five Type B thermocouples were also installed. To verify the new temperature profile in the furnace an additional suction pyrometer test was conducted.

Again, an initial firing rate of 67,500 Btu/hr (19.8 kW) while burning propane was tried. The results are plotted in Figure 6. As compared to conditions under Phase I, the temperatures are lower and the residence times of the gases increased. Although in an acceptable range, it was felt that by reducing the firing rate, the temperature window and residence time could be maximized for the furnace configuration.

A series of tests were therefore conducted at a lower firing rate of 47,300 Btu/hr (14 kW) [3.5 lb/hr (0.44 g/s) coal]. Suction pyrometer testing was performed while burning propane at this firing rate and SR of 1.05, 1.15, and 1.25. The results of these tests are presented in Figure 7 and Table 2. In addition duplicate tests were performed at the same condition, SR of 1.25, on different days (see Table 2). The results are within ± 2 percent of each other for each port, and most of the temperatures are less than a half a percent different. This shows good reproducibility of results.

Suction pyrometer testing was also conducted while burning 3.5 lb/hr (0.44 g/s) of Pittsburgh #8 coal. Again, the air stoichiometric ratios were 1.05, 1.15, and 1.25. The results are presented in Figure 8 and Table 3. The procedures described in the previous section were modified because of plugging problems of the pyrometer with fly ash. From the original suction pyrometer tests (see Appendix B) it was determined that at least 15,000 lb/ft^2 hr (1,221 kg/m^{2}s) [2.0 scfm (94 µm^3/s) measured at the dry gas meter] must be pulled over the thermocouple junction to be in the flat (equilibrium) portion of the curve. At these relatively high volumes, the suction pyrometer would immediately plug with fly ash and/or molten ash. To eliminate the plugging problem, an efficiency of the suction pyrometer at a low flow rate was determined from the graphs in Appendix B. From these graphs, it was calculated that at 11,000 lb/ft^2 hr (895 kg/m^{2}s) [1.5 scfm (707 µm^3/s) flow on the dry gas meter] the pyrometer temperature was 98 percent of the equilibrium temperature. For the data in Figure 8, sampling was conducted at a flow rate of 11,000 lb/ft^2 hr (895 kg/m^{2}s) [1.5 scfm (707 µm^3/s)] and the resultant temperatures divided by 98 percent. At this lower flow rate plugging was not a problem.

Finally a series of tests were conducted to determine what effect burner design and the addition of sorbent injection air would have on the temperature versus residence time profiles. All previous data have been reported using the radial burner. During testing of the furnace it was determined that the axial burner will be the burner of choice for SO_2 reduction testing.

Axial Burner. Suction pyrometer tests were conducted with the axial burner and compared to the radial burner. In addition, another series of tests were conducted with the sorbent injection probe being inserted at a point approximately 32 inches (0.81 m) from the burner tip. Tests were conducted with each burner with and without sorbent air being injected at this point. Whenever sorbent air was injected into the furnace, the tangential air to the burner was reduced by the appropriate amount to keep the overall SR to 1.25. Results of the tests are presented in Table 4 and Figure 9. As can be seen from this data, there is only a slight difference in the observed temperatures for the two burners when all the air is added at the burner (only about 5 percent difference measured at each port). When sorbent air is added downstream of the burner, the observed temperaatures between the burners vary by about 10 percent. The effect of adding sorbent air lowers the measured temperature profile for each burner design.

The measured temperatures when adding sorbent air downstream of the burner are anywhere from 5 to 10 percent lower than adding the air at the burner. The farther away from the burner, the more uniform the temperatures become. The above tests were conducted at an SR of 1.25. An additional set of tests was conducted at an SR of 1.05 using the axial burner both with and without sorbent injection air. The results of these tests are plotted in Figure 10. As can be seen, at this SR, adding sorbent injection air at this point greatly reduces the peak temperatures near the flame, but has little effect on the temperatures farther down the furnace length. Temperature variations range from approximately 10 percent nearest the burner to less than 5 percent at the lower ports. Finally, Figure 11 is a plot of the range of temperatures versus residence time observed while firing propane with the axial burner. The hottest temperatures observed were while operating at an SR of 1.05 with sorbent air injected at the burner, while the coolest were at an SR of 1.25 with downstream sorbent air injection. These temperatures vary only from 13 to 6 percent; again, the temperatures converge as the distance from the burner increases.

CONCLUSIONS

From the data presented in the preceding sections, the following conclusions can be made.

- The original length of the furnace (Phase I) was not adequate to provide for a wide enough range of temperature/residence times for flexibility in testing limestone injection.
- Increasing the furnace length and operating at a firing rate of 47,300 Btu/hr (14 kW) [3.5 lb/h (0.44 g/s) coal] gives adequate residence times and temperature profiles for limestone injection testing.
- Lowering the stoichiometric ratio (excess air) produced the expected longer residence time. At lower air settings, the initial temperatures were hotter, while the bottom ports showed temperatures cooler than at a higher air setting. As can be seen from Figures 7 and 8, the temperature variations for the three excess air settings were small. The largest range of 200°F (93°C) occurred at the top port nearest the burner. In fact, the average temperature variation for propane (excluding the top two ports) is 63°F (18°C) while the average for coal is only 70°F (21°C). Therefore the SR can be assumed to have little effect on the temperature profile for this furnace when the entire volume of combustion air is mixed at the burner.
- The temperature profiles measured while burning coal and propane at the same Btu firing rate and SR also fall in a narrow range. The temperatures do not vary by more than 4 percent--except for one measurement at an SR of 1.05 at the point nearest the burner.
- The temperature profiles observed between different burner designs (axial vs. radial) were also very small, less than 5 percent, when all air is mixed at the burner. Temperature variation between burners was slightly higher when the sorbent air was added downstream of the burner--with the radial burner's temperatures being 6 to 13 percent cooler.

REFERENCES

1. Babcock and Wilcox, 1973. Steam/Its Generation and Use.
2. Benedict, R. P., 1977. Fundamentals of Temperature, Pressure, and Flow Measurements. John Wiley & Sons, New York.
3. EPA, Standards of Performance for New Sources: Revision to Reference Methods 1-8, Federal Register 42(160), 41776-41782, 1977.

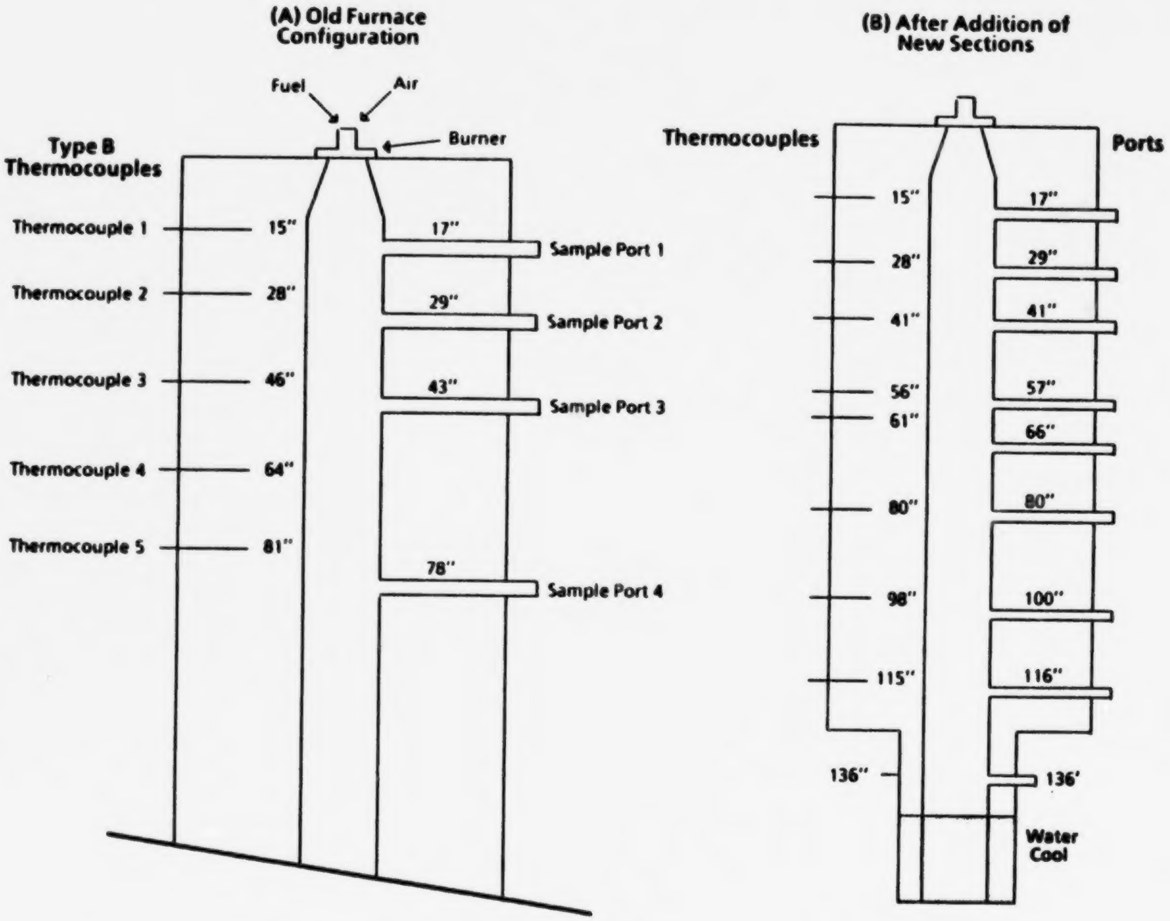
(A) Old Furnace Configuration
Fuel
Air
Burner
Type B Thermocouples
Thermocouple 1
Thermocouple 2
Thermocouple 3
Thermocouple 4
Thermocouple 5
15"
28"
46"
64"
81"
17"
29"
43"
78"
Sample Port 1
Sample Port 2
Sample Port 3
Sample Port 4
(B) After Addition of New Sections
Thermocouples
Ports
15"
28"
41"
56"
61"
80"
98"
115"
136"
17"
29"
41"
57"
66"
80"
100"
116"
136'
Water Cool

Figure 1. Diagram of LIMB furnace showing location of Type B thermocouples and sampling ports.

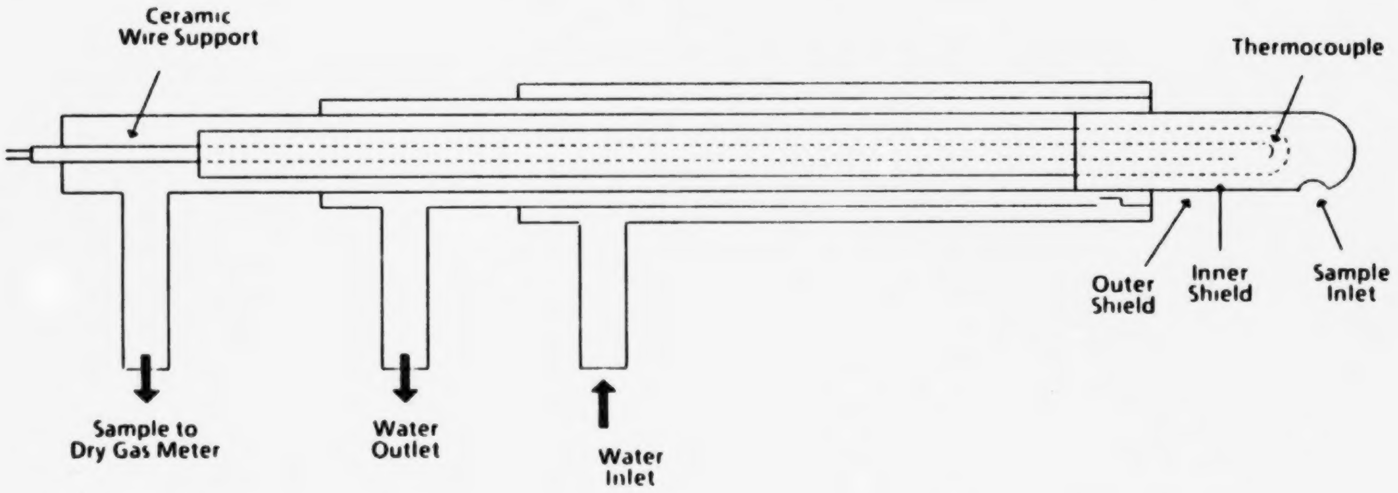
Ceramic Wire Support
Thermocouple
Outer Shield
Inner Shield
Sample Inlet
Sample to Dry Gas Meter
Water Outlet
Water Inlet

Figure 2. Cross section of water cooled suction pyrometer.

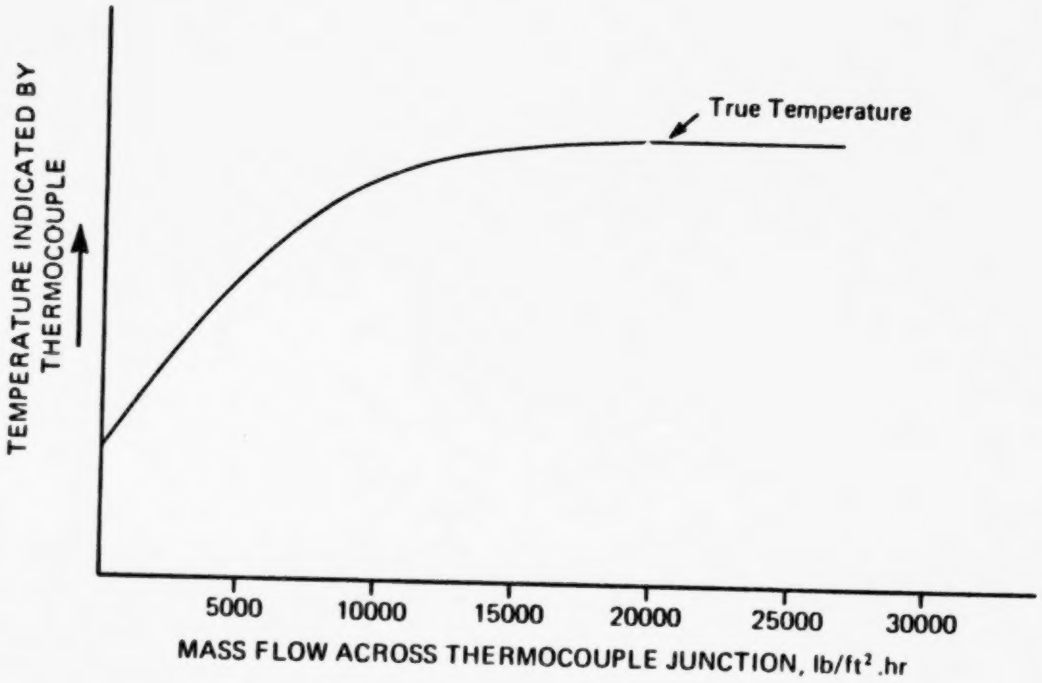

Figure 3. Effect of gas mass velocity on measured temperature.

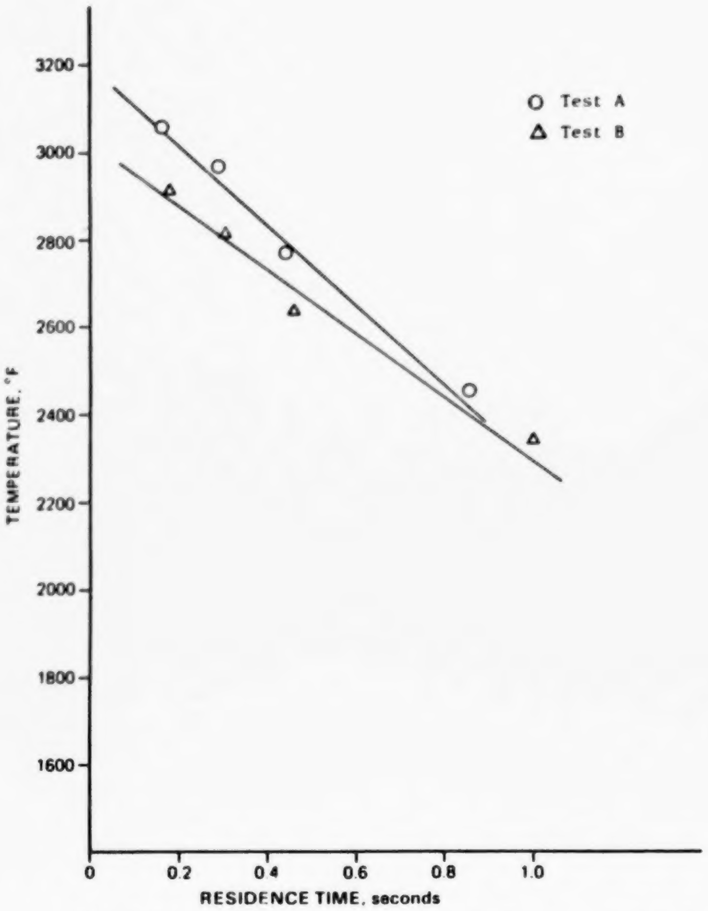

Figure 4. Temperature vs. residence time under Phase I at a propane firing rate of 67,500 Btu/hr (5.0 lb/hr coal).

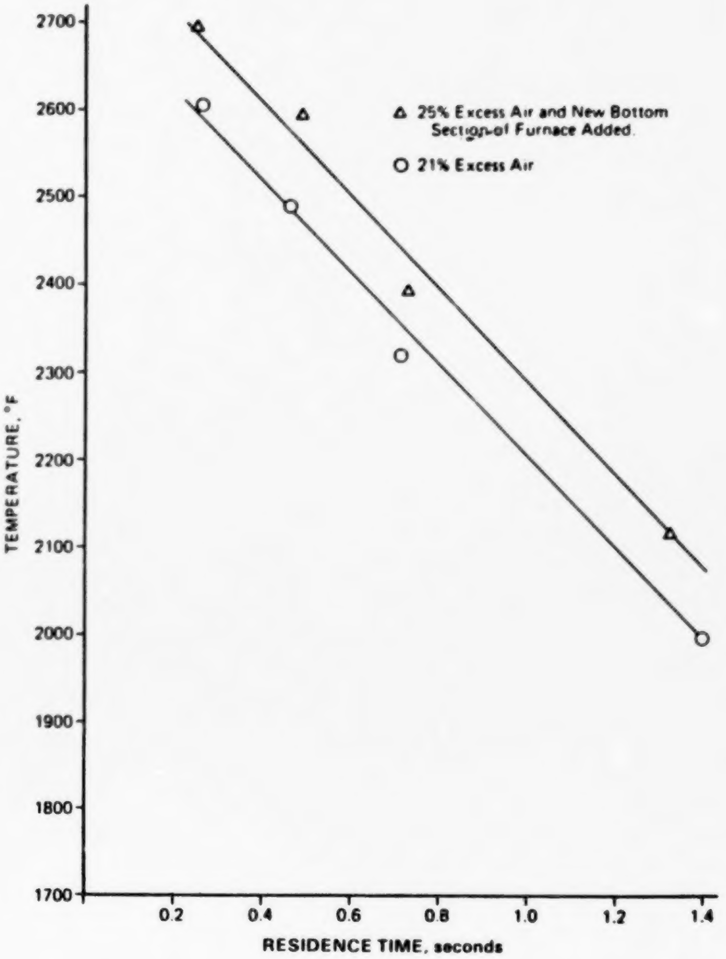

Figure 5. Temperature vs. residence time under Phase I at a propane firing rate of 47,300 Btu/hr (3.5 lb/hr coal).

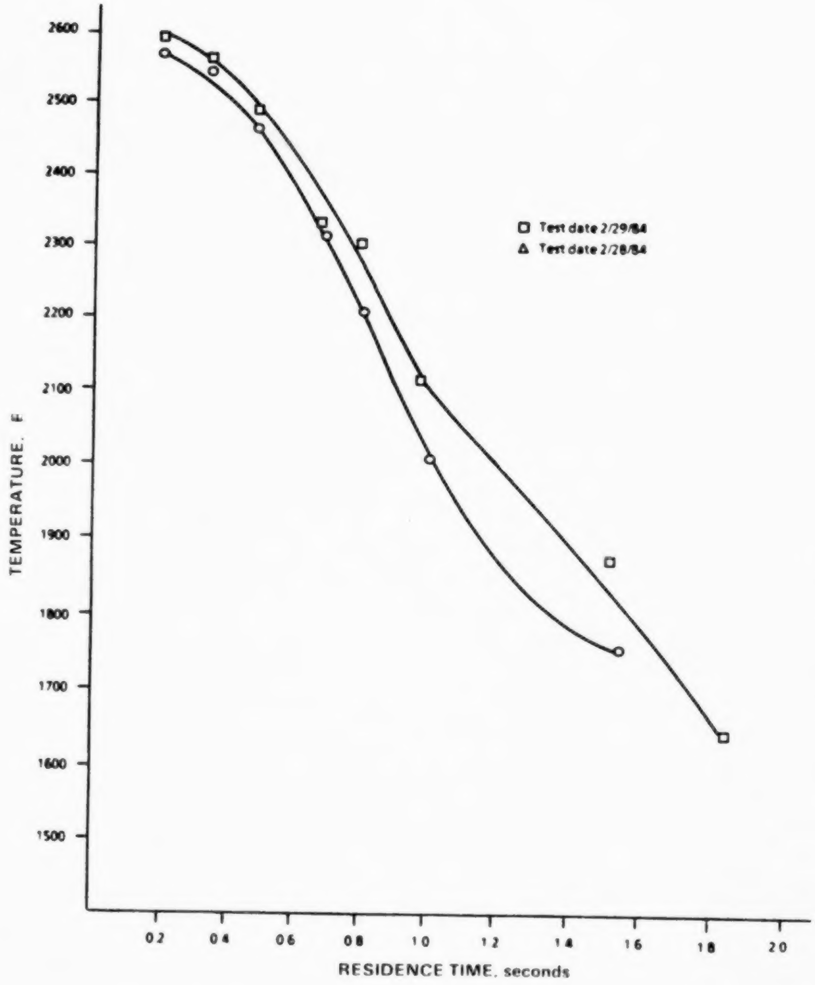

Figure 6. Temperature vs. residence time at a firing rate of 67,500 Btu/hr propane and SR of 1.15.

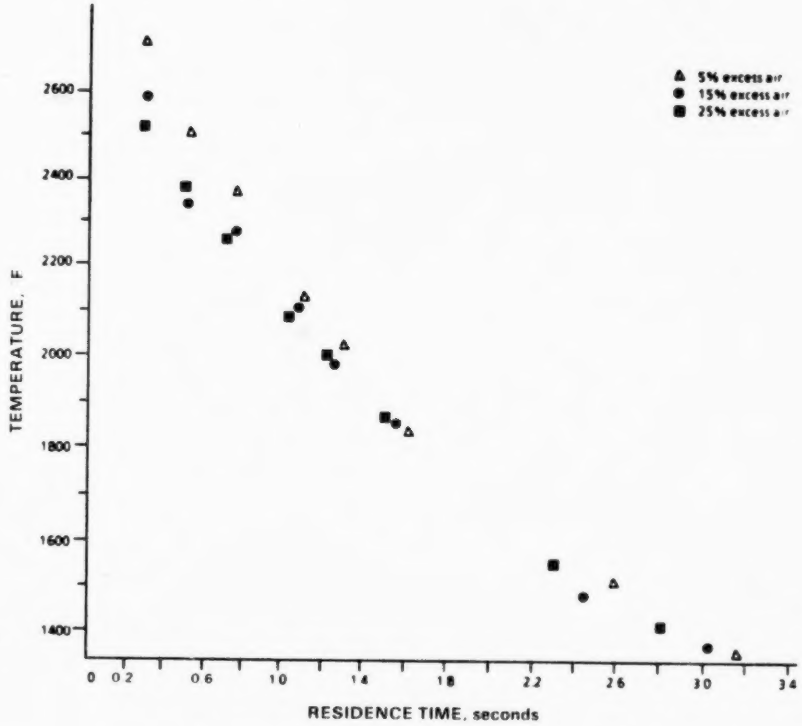

Figure 7. Temperature vs. residence time profiles at a firing rate of 47,300 Btu/hr propane.

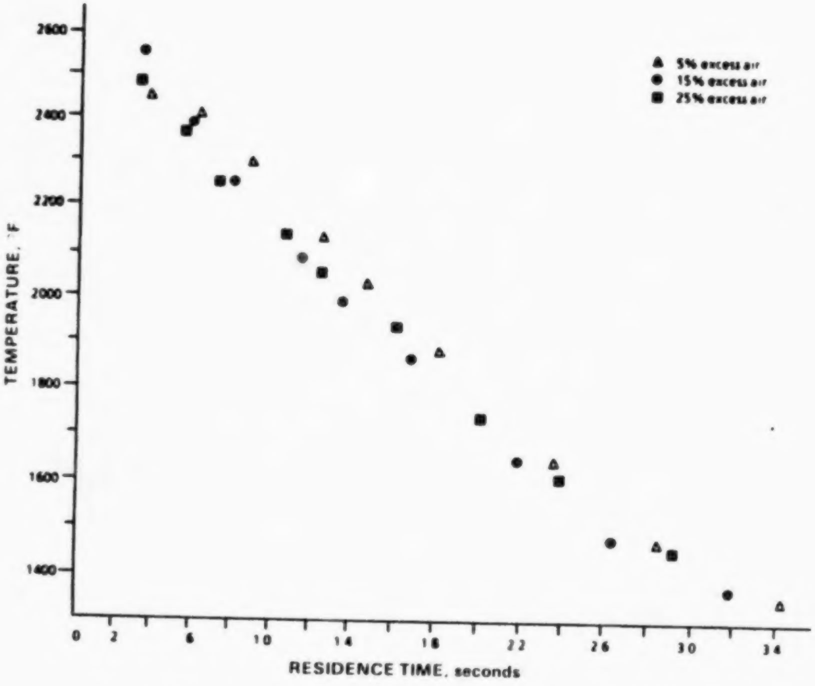

Figure 8. Temperature vs. residence time profile burning 3.5 lb/hr coal (47,300 Btu/hr).

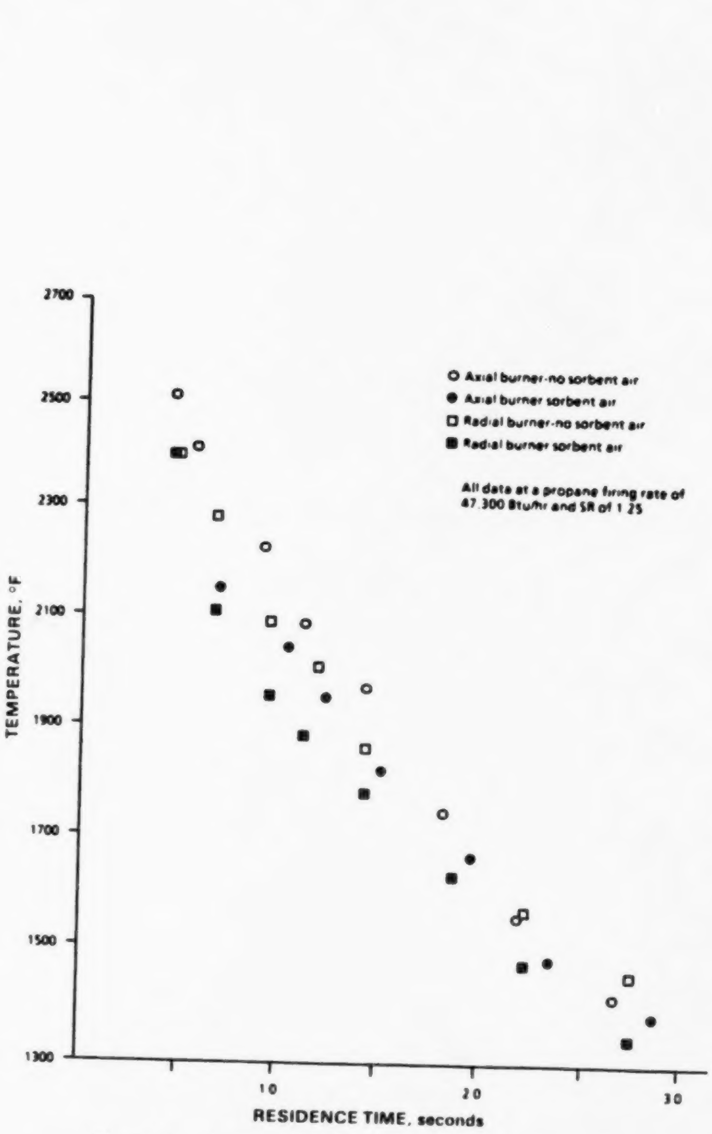

Figure 9. Comparison of axial vs. radial burner both with and without adding sorbent air downstream of the burner.

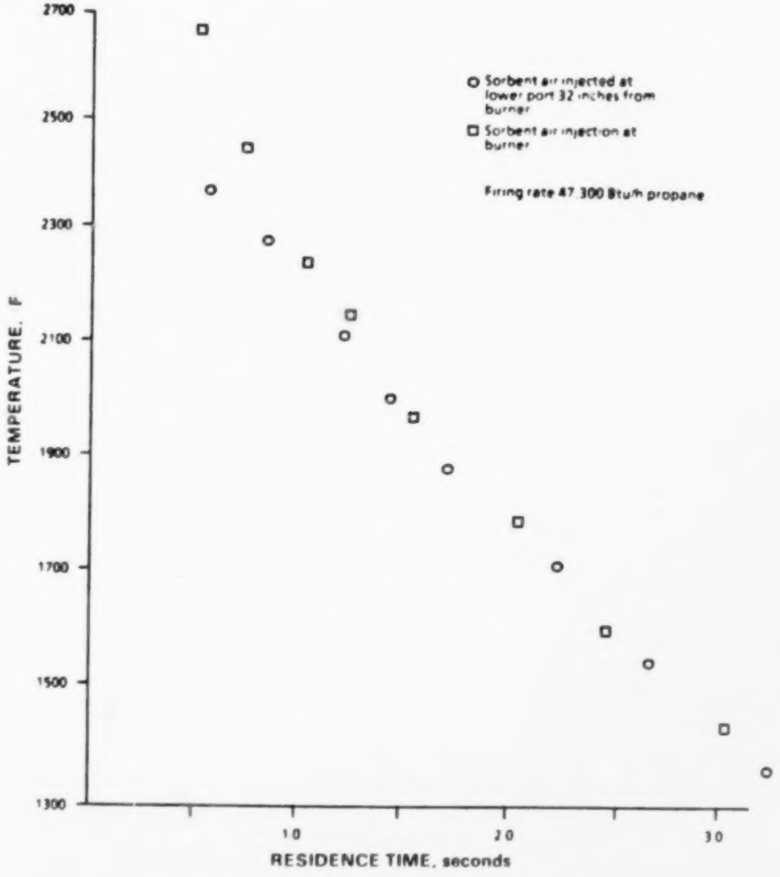

Figure 10. Effect of adding sorbent air downstream of the axial burner at an SR of 1.05.

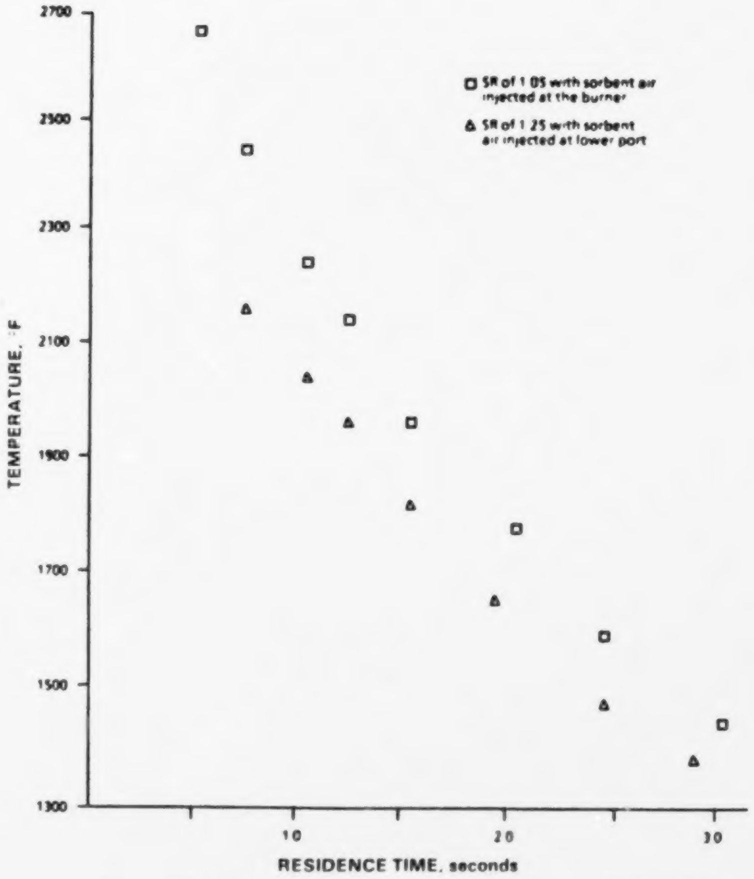

Figure 11. Temperature range for axial burner firing at a rate of 47,300 Btu/hr of propane.

Table 1

SUCTION PYROMETER DATA CONDUCTED IN THE LIMB FURNACE UNDER PHASE I

Distance From Burner (inches)	67,500 Btu/hr SR* 1.10 10/19-10/24/83		67,500 Btu/hr SR 1.10 11/1/83		47,300 Btu/hr SR 1.25 11/8/83		47,300 Btu/hr SR 1.25 1/23/84	
	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)
17	3,060	0.167	2,908	0.174	2,604	0.268	2,694	0.300
29	2,880	0.288	2,713	0.300	2,374	0.468	2,489	0.489
43	2,660	0.438	2,565	0.456	2,264	0.711	2,293	0.725
78	2,250	0.854	2,127	1.00	1,497	1.398	1,937	1.325

* SR = Stoichiometric ratio of combustion air to fuel

Table 2

SUCTION PYROMETER TESTS BURNING PROPANE AT 47,300 BTU/H* USING THE RADIAL BURNER

Distance From Burner (inches)	SR of 1.15 3/1/84		SR of 1.25 3/2/84		SR of 1.05 3/5/84		SR of 1.25 3/6/84	
	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)
17	2,574	0.29	2,503	0.277	2,709	0.303	2,538	0.273
29	2,336	0.505	2,370	0.477	2,510	0.524	2,404	0.470
41	2,264	0.732	2,251	0.686	2,376	0.758	2,287	0.676
57	2,104	1.048	2,080	0.980	2,137	1.091	2,089	0.967
66	1,982	1.236	1,994	1.193	2,036	1.291	2,006	1.140
80	1,849	1.543	1,861	1.476	1,850	1.620	1,864	1.421
116	1,500	2,423	1,566	2.276	1,535	2.565	1,564	2.218
136	1,397	2.97	1,435	2.768	1,373	3.156	1,464	2.706

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* Equivalent to 3.5 lb/h coal

Table 3

SUCTION PYROMETER TESTS BURNING 3.5 LB/H COAL* USING THE RADIAL BURNER

	SR of 1.25 3/16/84		SR of 1.05 3/19/84		SR of 1.15 3/20/84	
Distance From Burner (inches)	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)
17	2,492	0.30	2,457	0.35	2,563	0.31
29	2,370	0.52	2,420	0.60	2,390	0.54
41	2,260	0.74	2,302	0.86	2,221	0.78
57	2,138	1.05	2,139	1.22	2,087	1.12
66	2,052	1.23	2,030	1.43	1,966	1.32
80	1,933	1.59	1,877	1.78	1,858	1.65
100	1,731	1.97	1,648	2.32	1,646	2.15
116	1,605	2.36	1,474	2.80	1,476	2.59
136	1,451	2.88	1,363	3.44	1,376	3.18

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* 47,300 Btu/h

Table 4

SUCTION PYROMETER TESTS COMPARING BURNER DESIGN AND THE EFFECT OF ADDING SORBENT INJECTION AIR DOWNSTREAM OF BURNER

	Radial Burner, 7/5/84				Axial Burner, 7/3/84			
	Sorbent Air at Burner		Sorbent Air Downstream of Burner		Sorbent Air Downstream of Burner		Sorbent Air at Burner	
Distance From Burner (inches)	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)	Temp. (°F)	Cumulative Residence Time (sec.)
29	2,404	0.470	2,400	0.448			2,515	0.471
41	2,287	0.676	2,103	0.662	2,160	0.763	2,402	0.669
57	2,089	0.967	1,955	0.946	2,037	1.065	2,230	0.947
66	2,006	1.140	1,882	1.128	1,951	1.242	2,098	1.113
80	1,864	1.421	1,780	1.423	1,820	1.530	1,961	1.423
100	-	-	1,635	1.869	1,662	1.969	1,741	1.841
116	1,564	2.218	1,480	2.219	1,488	2.349	1,565	2.206
136	1,464	2.706	1,352	2.727	1,395	2.857	1,425	2.653
	Quench Rate = 467°F/sec		Quench Rate = 492°F/sec		Quench Rate = 417°F/sec		Quench Rate = 533°F/sec	

All data for an SR of 1.25, and firing propane at 47,250 Btu/hr

APPENDIX A
SAMPLE CALCULATIONS

1. The following calculations are for the data collected on January 23, 1984, while performing suction pyrometer testing on the LIMB furnace.

DATA

Propane flow rate - 0.36 cfm @ 0.5 psi
Tangential air flow - 4.5 cfm @ 45 psi
Pilot air flow - 50.0 cfh @ 15 psi

CO_2 - 10.64%
O_2 - 4.325% (concentrations are measured on a dry basis)
CO ≈ 0

Using radial burner

A. Computing actual scfm of propane burned

$$\text{Actual scfm of propane burned} = 0.868 \times \text{rotometer setting} \times \text{pressure correction} + 0.024$$

$$= (0.868 \times 0.36) \times \sqrt{\frac{14.7 + 0.5}{14.7}} + 0.024$$

$$= 0.34 \text{ scfm}$$

$$\text{Btu/hr} = 0.34 \frac{\text{scf}}{\text{min.}} \times 2322 \frac{\text{Btu}}{\text{scf}} \times \frac{60 \text{ min.}}{\text{hr}} = 47{,}368 \text{ Btu/hr}$$

B. Total volume of air metered into burner

$$\text{Tangential air} = \text{rotometer setting} \times \text{pressure correction}$$

$$= 4.5 \times \sqrt{\frac{14.7 + 45}{14.7}}$$

$$= 9.0 \text{ scfm}$$

$$\text{Pilot air} = \text{rotometer setting} \times \text{pressure correction} \times \frac{\text{hr}}{60 \text{ min.}}$$

$$= 50 \text{ cfh} \times \sqrt{\frac{14.7 + 15}{14.7}} \times \frac{1}{60}$$

$$= 1.18 \text{ scfm}$$

Total air

$$\begin{array}{lr} \text{Tangential} = & 9.00 \\ \text{Pilot} = & \underline{1.18} \\ & \overline{10.18} \text{ scfm} \end{array}$$

O_2 = 0.21 x 10.18 = 2.14 scfm
N_2 = 0.79 x 10.18 = 8.04 scfm

C. Excess air calculations

$$\text{Theoretical air required at 0\% excess} = \frac{\text{23.82 cubic feet air}}{\text{cubic feet of propane}} \times \text{actual scfm propane burned}$$

$$= 23.82 \times 0.34 = 8.1 \text{ scfm of air}$$

Excess Air from Rotometers

Rotometers = 10.18 scfm
Theoretical = 8.1 scfm

$$\text{\% Excess air} = \frac{10.18}{8.1} = 1.257$$

$$= 25.7\%$$

Theoretical O_2 at 0% EA = 8.1 x 0.21 = 1.7

O_2 metered in = 2.14 scfm
theoretical = 1.7
excess O_2 = 0.44 scfm

Excess Air from Monitors

O_2 = 4.375%
CO_2 = 10.64%

% Excess air = 23.6%

D. Total Volume of Flue Products

$$CO_2 = \frac{3.0 \text{ ft}^3}{\text{ft}^3 \text{ of propane burned}}$$

$$H_2O = \frac{4.0 \text{ ft}^3}{\text{ft}^3 \text{ of propane burned}}$$

Total Volume of Flue Gases

CO_2 = 3.0 x 0.34 = 1.02
H_2O = 4.0 x 0.34 = 1.36
N_2 = (from B) = 8.04
Excess O_2 = (from C) = 0.44
10.86

E. Residence Time

Area of furnace = πr^2

$= \pi\ (3/12)^2$

$= 0.196\ ft^2$

1. Residence time from burner to Port 1, T = 2694°F and L = 17 inches or 1.42 ft

   Velocity = total scfm x temperature correction x $\frac{1}{area}$ x $\frac{min}{60\ sec}$

   $$= 10.79 \times \frac{2694 + 460}{70 + 460} \times \frac{1}{0.196} \times \frac{1}{60} = 5.46\ ft/s$$

   Residence time = $1.42\ ft \times \frac{1}{5.46\ ft/sec} = 0.26\ sec$

2. Residence time from Port 1 (T = 2694°F) to Port 2 (T = 2489°F)

   Average T between ports = 2592°F
   Distance = 12 inches or 1 ft

   $$Velocity = 10.79 \times \frac{2592 + 460}{70 + 460} \times \frac{1}{0.196} \times \frac{1}{60} = 5.28\ ft/sec$$

   Residence time = $1\ ft \times \frac{1}{5.28\ ft/sec} = 0.189\ sec$

3. Residence time from Port 2 (T = 2489°F) to Port 3 (2293°F)

   Average T = 2391
   Distance = 14 inches or 1.17 ft

   $$Velocity = 10.79 \times \frac{2391 + 460}{70 + 460} \times \frac{1}{0.196} \times \frac{1}{60} = 4.94\ ft/sec$$

   Residence time = $1.17\ ft \times \frac{1}{4.94\ ft/sec} = 0.237\ sec$

4. Residence time from Port 3 (2293°F) to Port 4 (1937)

   Average T = 2115
   Distance = 35 inches or 2.92 ft

   $$Velocity = 10.79 \times \frac{2115 + 460}{70 + 460} \times \frac{1}{0.196} \times \frac{1}{60} = 4.46\ ft/sec$$

   Residence time = $2.92\ ft \times \frac{1}{4.46\ ft/sec} = 0.655\ sec$

APPENDIX B

SUCTION PYROMETER CURVES OF TEMPERATURE VERSUS MASS FLOW RATE

The following figures are the temperature versus mass flow rate curves developed for the suction pyrometer used in testing the LIMB furnace. Curves were developed at each sampling port. All tests were conducted at the following conditions:

Firing Rate = 67,500 Btu/hr propane
Excess Air = 10%
Inner diameter of the shield = 1/2-inch
Outer diameter of the sheath = 3/8-inch

The following conversion was used to convert the scfm measured at the dry gas meter to units of lb/hr ft^2 of mass flow over the thermocouple junction:

$$\text{scfm at dry gas meter} \times \frac{\text{moles}}{\text{scf}} \times \frac{\text{lb}}{\text{mole}} \times \frac{\text{min}}{\text{hr}} \times \frac{1}{\text{area between inner and outer ceramics}}$$

$$1.0 \text{ scfm} \times \frac{\text{moles}}{387 \text{ scf}} \times \frac{29 \text{ lb}}{\text{mole}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{1}{(0.15 \text{ in}^2 - 0.11 \text{ in}^2) \dfrac{\text{ft}^2}{144 \text{ in}^2}}$$

$$\text{1 scfm at dry gas meter} = 7{,}598 \text{ lb/ft}^2 \text{ hr}$$

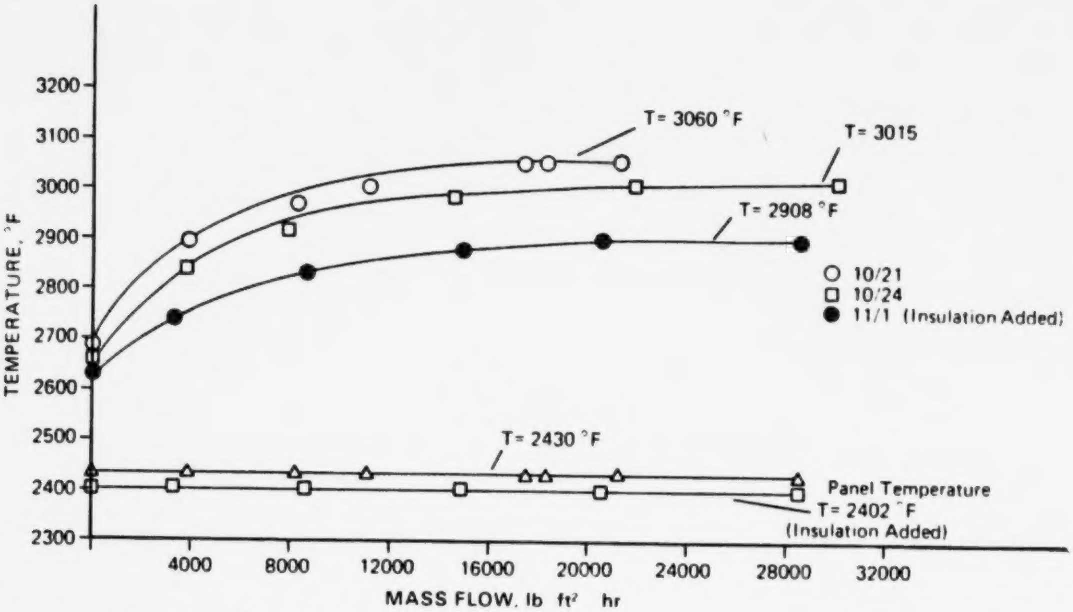

Figure B-1. Results of tests at Port No. 1--17 inches from burner.

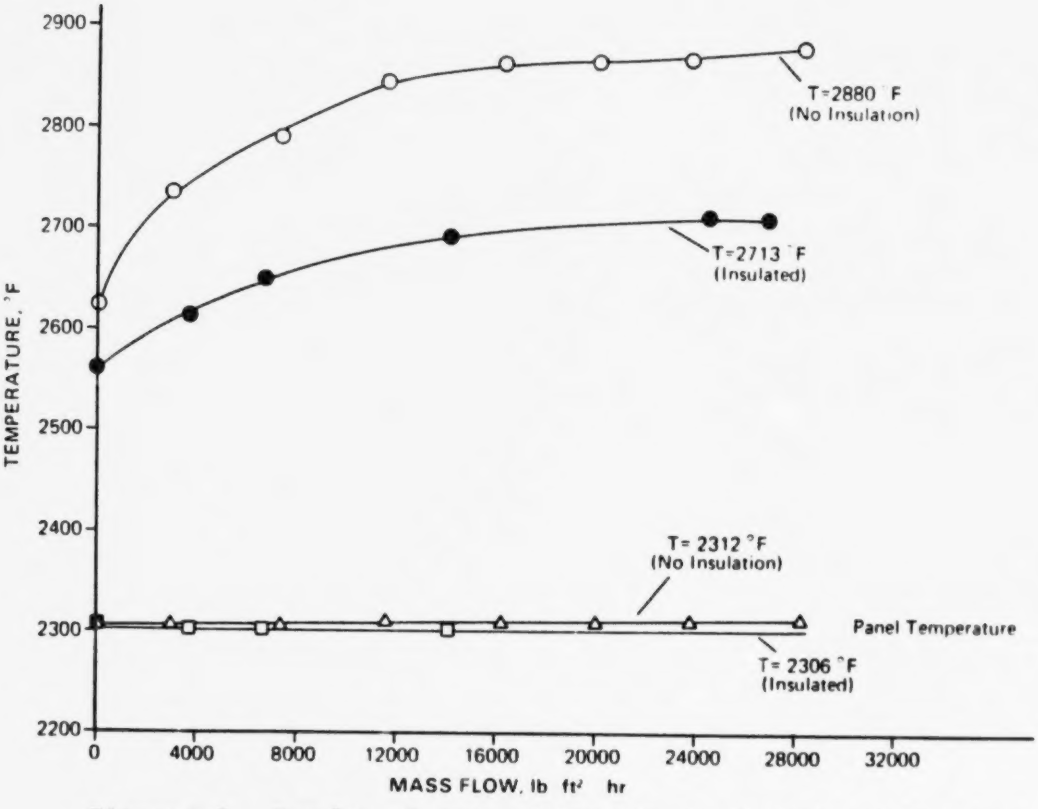

Figure B-2. Results of tests at Port No. 2--29 inches from burner.

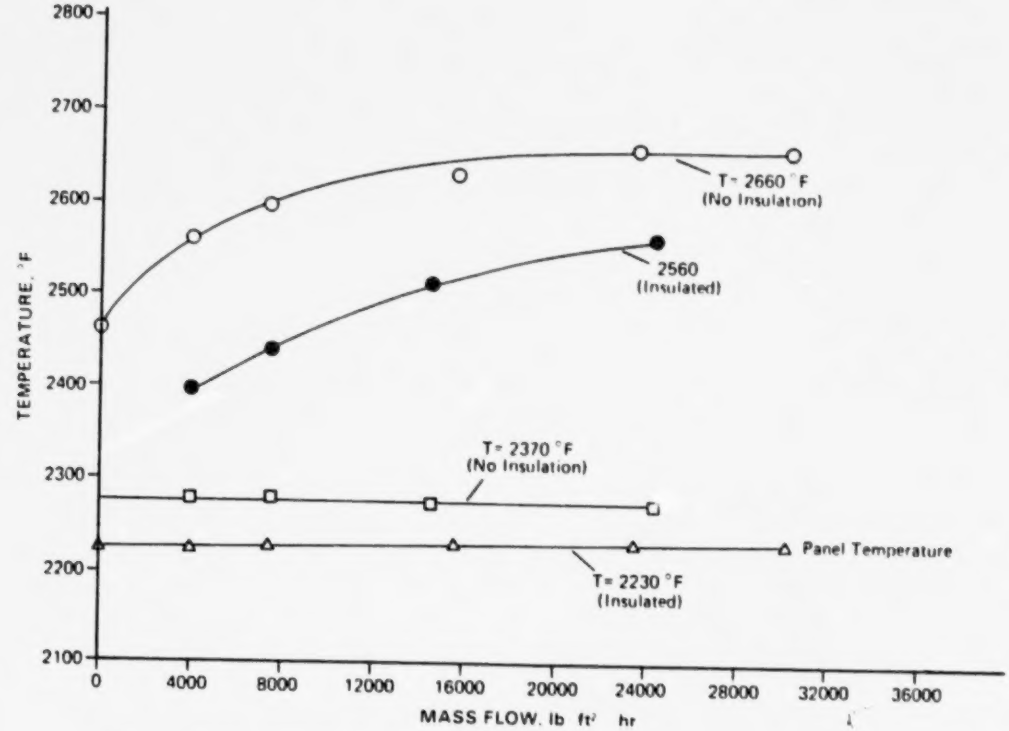

Figure B-3. Results of tests at Port No. 3--43 inches from burner.

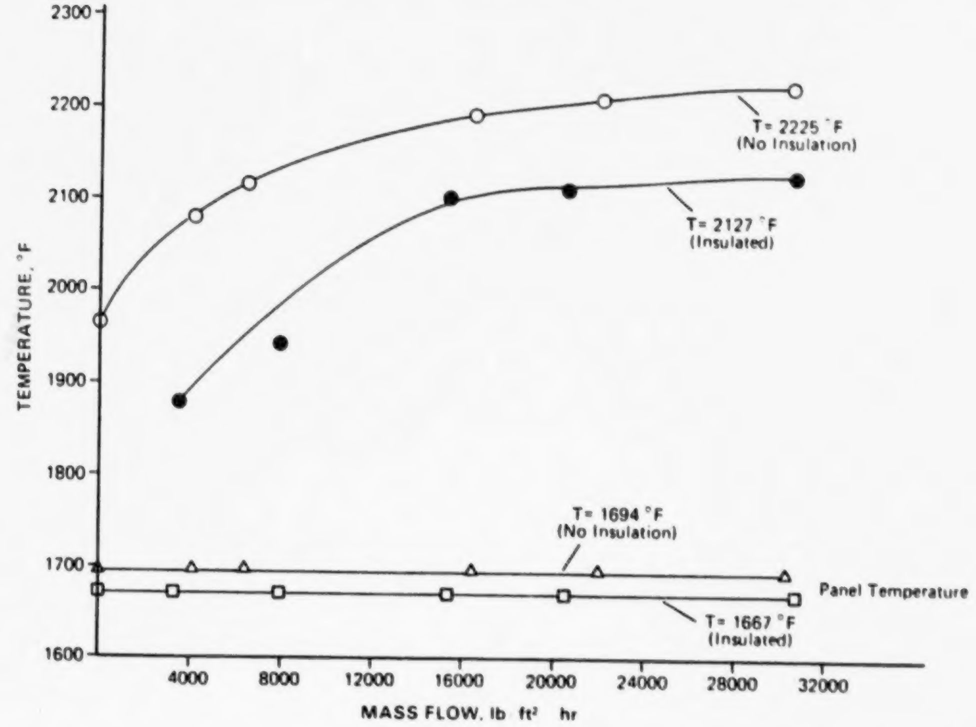

Figure B-4. Results of tests at Port No. 4--78 inches from burner.

(Unpresented Paper)

SURFACE CHARACTERIZATION AND MICROANALYSIS OF SORBENTS AND ASH/SORBENT MIXTURES

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ABSTRACT

This paper presents a survey of techniques for the surface characterization and microanalysis of particulate samples related to EPA's Limestone Injection Multistage Burner (LIMB) program. The following techniques are discussed: scanning electron microscopy (SEM), carbon replica transmission electron microscopy (TEM), thin section TEM, energy dispersive X-ray (EDX) analysis, electron microprobe analysis (EMA), electron spectroscopy for chemical analysis (ESCA), and Auger electron spectroscopy (AES). Example applications of these techniques to various LIMB samples are presented, and the limitations of the techniques are discussed.

SEM was found to be particularly useful in elucidating the surface morphology of calcines and sulfated calcines. In several photomicrographs, the pore openings in the calcines appeared to be slit-like and the calcination appeared to be directionally controlled. Carbon replica TEM was found to be tedious and unwarranted in view of the success with SEM. Thin section TEM may be useful in elucidating internal particle structure if a nondestructive sectioning technique can be developed.

EDX in conjunction with SEM was found to be quite useful in investigating the relative abundance of various elements in different samples as well as the distribution of a given element within a field of particles. The electron microprobe was useful for studying variations in elemental intensities in the top 4-5 μm of a 20-μm region of a sample. Due to poor spatial resolution, ESCA was found to be unsuitable for heterogeneous particulate mixtures. Elemental depth profiles in individual particles can be determined by AES coupled with ion milling. The results, however, are very sensitive to particle charging effects and particle topography.

SURFACE CHARACTERIZATION AND MICROANALYSIS OF SORBENTS AND ASH/SORBENT MIXTURES

INTRODUCTION

Program Needs

The developmental stage of EPA's LIMB (Limestone Injection Multistage Burner) program includes the need for a variety of analytical techniques applicable to the process inputs and products. While methods for bulk quantitative elemental analysis, mineral identification, and gross physical characterization are generally available and appear to be appropriate for LIMB materials, the applicability of microanalytical techniques to the assessment of particle composition and structure is far less certain. Particles in the micron size range and structures in the submicron range are frequently of interest. The three LIMB process considerations which provided the principal foci for this survey of analytical techniques are: a) high surface area sorbents; b) ash/sorbent interaction products; and c) sulfation products.

Recently, it has been recognized that the LIMB process may be made more efficient by injecting precalcined sorbents downstream from the coal burner. This is in sharp contrast to the original concept of the process which involved the injection of limestone through the burner. These externally produced sorbents may consist of calcines, hydrates, pressure hydrates, or chemically enhanced forms of these materials. The kinetic information presently available on the sulfation stage of the process suggests that these materials should have high surface areas to enhance sulfur capture (1). It suggests further that this surface area, to the extent that it is concentrated in the internal porosity of the sorbent particles, must be distributed among the coarser pore sizes to retard blockage by reaction products.

The nitrogen adsorption technique employed in BET (Brunauer, Emmett, and Teller) analysis can determine surface area directly while multipoint BET analysis will permit the derivation of pore volume and radii. Similarly, mercury porosimetry analysis will measure pore volume directly, with surface area and pore size being derived values. The accuracy of these derivations rely on a set of assumptions, one of which is that the pores involved are cylindrical in shape. To investigate the validity of this assumption and the resulting analyses, it is desirable to identify a technique by which the pores of sorbent particles can be directly observed.

The second recent development which has provided incentive for this study is the realization that certain elemental and/or mineralogic components of the mineral matter contained in the coal fuel can either enhance or retard the ability of sorbents to capture sulfur during the combustion process. Different types of sorbents appear to be affected to varying degrees by this interaction. Principal mechanisms hypothesized for the interaction include vaporization/condensation and collision/adhesion. Although speculation and theory have been marshalled by proponents of both views, no compelling empirical evidence has been put forth. Since the interaction phenomenon can determine the efficacy of the LIMB process, the mechanism and components involved must be identified. At least three different types of microanalytical procedures appear to be applicable to this area: 1) one which will allow visualization of the structure and relative proportions of different types of particles; 2) one which will permit whole particle elemental analysis; and 3) one designed for depth-profile or cross-sectional elemental analysis of individual particles.

The third area to derive a potential benefit from this survey is the study of sulfated products from the LIMB process. Efforts are currently being directed toward the development of models to simulate the mechanism of sulfation. Interpretation of experimental evidence supporting this model development suggests that the sulfation reaction is controlled by diffusion of SO_2 through the product layer created on the sorbent (2). Presently, however, not all aspects of the various models are in agreement, nor are results from furnace experiments always adequately predicted by the models. To assist in the resolution of these disparities, it seems reasonable to employ visualization techniques to determine if closure or restriction of pores by product layers is actually occurring. A similar purpose might be achieved by measuring elemental depth profiles or cross sections of individual sulfated sorbent particles.

Study Objectives and Scope

The objective was to identify a set of microanalytical techniques which, when employed within the framework of a well-designed sampling and experimental plan, would be appropriate for application to the materials involved in the three process areas described above. In and of itself the study was not designed to resolve these problems.

Specifically, the survey was to identify: 1) visualization techniques capable of accurately portraying particle morphology and structures down to the submicron size range; 2) methods of elemental identification and quantification in whole particles down to a few microns in size; 3) methods of quantifying elemental content in depth profiles or cross sections of particles down to a few microns in size; and 4) the sample preparation techniques accompanying these analyical methods appropriate for application to LIMB-related materials. Excluded from the survey were bulk elemental quantification analyses, mineral identification methods, and techniques for gross physical characterization. Also excluded were surface area, pore volume, and pore size analyses. The available BET and mercury porosimetry techniques are believed to have been adequately tested for accuracy and precision through the analysis of standards, and intralaboratory and interlaboratory comparisons.

VISUALIZATION TECHNIQUES

Scanning Electron Microscopy

Scanning electron microscopy (SEM) may be used to study the size, shape, and surface morphology of LIMB-related samples. The size and shape of the particles can generally be studied using any production-grade SEM that is in good operating condition. However, a research-grade SEM that is capable of high resolution (~30 Å)* is required for study of some of the intricate surface features of LIMB particles. Both types of SEM's have been used in this study. The production-grade instrument was an ETEC Autoscan automatic scanning electron microscope. The manufacturer's maximum resolution is about 200 Å, which limits the maximum useful magnification to about 20,000X when a good specimen is imaged. The research-grade instrument used in this study was a Camscan Series 4 SEM. This instrument has a maximum resolution of about 30 Å, which limits the maximum useful magnification to approximately 120,000X.

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*10,000 Å = 1 μm.

For morphological studies of the particulate surface, exposure of the sample to the atmosphere must be minimized. The surface morphology of LIMB sorbent particles can be drastically altered by the pickup of H_2O and CO_2 from ambient air. These effects have been strongly suspected during recent examinations of hydrated lime particles and calcines produced therefrom.

A variety of techniques may be employed to prepare particulate samples for SEM examination (3). The prime considerations are: (a) to make the particles electrically conductive so that particle charging effects will not interfere with the examination; and (b) to avoid obscuring any of the surface details of the particles. Of course, the latter consideration is important only when the objective is to study the detailed surface morphology as opposed to the general size and shape of the particles. In order to make the particles conductive, they may be pressed into a metal foil or coated with a thin layer of carbon or a metal (e.g., gold, platinum/paladium, or silver). For high-resolution work, a thin (<20 Å) gold coating has been found to yield good results. The use of gold can be a problem, however, if the sample that is being imaged is to be simultaneously analyzed by an energy dispersive X-ray (EDX) attachment on the SEM. Gold interferes with sulfur in the EDX spectrum. Therefore, a gold coating should not be used when planning to analyze sulfated sorbent samples by EDX. A silver coating was used for most of the EDX work performed in this study.

In this study, the SEM was used to examine a number of different LIMB-related samples including:

(1) 3-5-cm hand samples of raw limestone rocks,

(2) limestone powders produced by crushing and pulverizing the rock,

(3) specific size fractions of powders produced in (2), above,

(4) calcines produced from the powders by heating in a controlled laboratory environment,

(5) a calcine produced by injection of a pulverized limestone into the burner of a natural-gas-fired furnace,

(6) a sulfated calcine produced under the same conditions as (5), above, except that the natural gas was doped with SO_2,

(7) an ash/sulfated calcine mixture produced under the same conditions as (5), above, except that the fuel was a medium (2%) sulfur coal instead of SO_2-doped gas,

(8) a hydrated lime—$Ca(OH)_2$—produced from one of the limestones in (2), above,

(9) a calcine and a sulfated calcine produced from the hydrated lime by downstream injection into a natural-gas-fired combustor with and without SO_2 doping,

(10) an ash/sulfated calcine mixture produced by downstream injection of the hydrated lime while firing the same coal used in (7), above, and

(11) reagent-grade calcite calcined under laboratory-scale conditions.

Samples (1)-(4) and (8)-(11), above, were examined on the Camscan research-grade SEM, while Samples (5)-(7), above, were examined on the ETEC production-grade SEM.

The same two limestones were used as the source materials for samples (1)-(4), above. The compositions of these two limestones are summarized in Table 1. The Longview limestone was supplied by Southern Industries, Inc., from their quarry located in Saginaw, Alabama, just south of Birmingham. The Maysville limestone was supplied by Dravo Lime Company from their quarry in Maysville, Kentucky, just south of Cincinnati, Ohio. A hand specimen of the Longview stone is gray-white in color, while the Maysville stone is pale-tan-to-buff colored with 0.8- to 3-mm thick bands of widely spaced dark brown material. Petrographic examinations show that the grain sizes range from 100 to 830 μm in the Longview stone, while most of the Maysville stone consists of microcrystalline calcite with an average grain size of 3 μm. The Maysville stone also contains sparite grains (~20 μm mean size) as well as dolomite rhombs (~50 μm mean size). A significant number of fossil fragments were found in the Maysville stone; whereas, the Longview stone was free of fossil fragments. The chemical analyses given in Table 1 show that the Maysville stone is significantly higher in dolomite content than the Longview stone. This was also indicated by X-ray diffraction analyses that showed only a trace (<3%) of dolomite in the Longview stone and a minor amount (3-10%) in the Maysville stone.

The two limestones described above were of interest in this study because calcines prepared from the same size fractions of the two crushed limestones under the same conditions had markedly different BET surface areas. For example, a 63- to 88-μm size fraction of the crushed Longview limestone yielded a calcine with a BET surface area of 51.2 m^2/g, while the same size fraction of the crushed Maysville stone yielded a calcine with a BET surface area of 39.8 m^2/g. These calcines were prepared by heating the limestone powder at 750°C for 30 min. The powder was dispersed on quartz wool and heated over flowing nitrogen. The raw stones, their powders, and their calcines were examined by SEM in an effort to identify any differences that might help explain the difference in BET surface areas. Photomicrographs of these materials are shown in Figures 1-6. Due to space limitations, only one of the size fractions (63-88 μm) of the crushed material is shown here, together with the corresponding calcine produced from the powder.

Figures 1 and 4 show that both the Longview and Maysville stone chips have a rough surface texture with many small (<10 μm) fragments adhering to the surface. An apparent grain boundary may be seen in the 2000X photograph of the Longview stone. The crushed powders, shown in Figures 2 and 5, consist of numerous particles that appear to be too large (>88 μm) along one axis, but about the right size (63-88 μm) along the other axis. This suggests that the particles were aligned with their major axes perpendicular to the sieve when the size cut was prepared. The net effect is particles that are larger than expected in one direction. The photomicrographs of the calcines produced from these powders (Figures 3 and 6) reveal the apparent production of cracks and fissures in the particle surface. Some of these cracks and fissures appear to be as large as 1 μm. However, there may be many other such features that are too small to see at this magnification. Given the very large specific surface areas of the calcines (51.2 m^2/g for the Longview and 39.8 m^2/g for the Maysville), it is clear that these materials must have considerable internal porosity that is accessible from the particle exterior. This is confirmed qualitatively in Figures 3 and 6. The purpose of Figures 1-6 is simply to illustrate the types of results that can be obtained by SEM. No serious attempt has been made to relate these results to any physical or chemical characteristics of the materials.

The photomicrographs discussed above were taken at relatively low magnifications (100X and 2000X). Such low magnifications are often adequate for studying the size and shape of particles or their general surface features; however, much higher magnifications are required to elucidate some of the intricacies in the surface morphology of calcines. This is illustrated in Figure 7 which shows two SEM photomicrographs of a calcine produced by heating reagent-grade calcite at 725°C for 30 min. The calcite particles were dispersed on quartz wool and heated over flowing nitrogen. This produced a calcine with a BET surface area of 27.6 m^2/g. The SEM photomicrographs of this material shown in Figure 7 reveal a surface morphology that is similar to that of ground beef. The surface is covered with creases or crevices that appear to be the openings of slits which penetrate below the particle surface. There is also an indication that the calcination is controlled directionally by twin planes within the crystal structure.

Figure 8 shows two other SEM photomicrographs of the same material shown in Figure 7. These two additional photographs are shown to illustrate the directional nature of the calcination process that is suggested by the surface morphology. They also tend to accentuate the fissure-like nature of the pore structure.

The SEM was also used to examine particles of hydrated lime—$Ca(OH)_2$—and the various calcination and sulfation products of this material. The following samples were examined:

(1) Commercial hydrated lime—$Ca(OH)_2$—made from the Longview limestone described previously.

(2) Calcine—CaO—produced by injecting the above into a natural-gas-fired furnace at about 1200°C with no SO_2 present.

(3) Sulfated calcine—$CaSO_4/CaO$—produced by injecting the hydrated lime at the same location but with the natural gas doped with 2190 ppm of SO_2.

(4) Sulfated calcine/ash mixture produced by injecting the hydrated lime at the same location but with Indiana 2% sulfur coal being fired.

SEM photomicrographs of these materials are shown in Figures 9-12. A comparison of Figures 9 and 10 reveals a pronounced change in the surface morphology due to calcination. Numerous openings are evident on the calcine surface which were not present in the raw material. In the 38,000X photograph of the calcine, there appear to be "holes" that are on the order of 400-1000 Å in size. Slits as small as 200 Å in width can also be resolved. The sulfated calcine particles shown in Figure 11 appear to be quite similar to the calcine particles before sulfation. In the fly ash/sulfated calcine mixture, some fly ash particles can be seen that appear to be coated with smaller sorbent or ash fragments as evident at 40,000X in Figure 12.

Transmission Electron Microscopy

The transmission electron microscope (TEM) may also be used to study the surface morphology of particles using a process called carbon replication (4). The procedure for preparing a carbon replica may be outlined as follows: (a) the particles in the sample are dusted onto a copper TEM grid that has been coated with a sticky, plastic-like Formvar film; (b) the particles are coated with a thin film of carbon in an evaporative coater; (c) the carbon coating is "shadowed" by deposition of a heavy metal (e.g., platinum/paladium) at an angle of about 10°; (d) the Formvar is dissolved and carried away by partially immersing the TEM grid in a shallow pool of chloroform; (e) the particles are dissolved and carried away by partially immersing the TEM grid in a shallow pool of dilute hydrochloric acid. This procedure leaves behind a thin carbon shell that is a precise replica of the original particle surface. The shadowing effect of the heavy metal emphasizes the surface features. Thus, the shadowed replica provides a "relief map" of the particle surface. While the use of carbon replica TEM offers the potential for detailed studies of surface morphology, practical problems make it difficult to consistently produce reliable carbon replicas. It was often difficult or impossible to completely dissolve the particles under the carbon coating. If the particles were completely dissolved, the carbon replica would frequently collapse because it was either too thin or because it spanned an unsupported area that was too large. With considerable care, however, it was found that good carbon replicas could be produced. Two such replicas are shown in Figure 13. These are replicas of calcine particles produced by heating reagent-grade calcite at 850°C for 30 min. The calcite particles were dispersed on quartz wool and heated in a static air environment. The calcine had a BET surface area of 18.7 m^2/g. The replicas of this material reveal numerous structural features on the particle surface that may account for some of the measured surface area, although the apparent porosity shown by the SEM photos is not clearly distinguishable.

The TEM may also be used to examine the internal structure of particles using a procedure called "thin sectioning" (5). A thin section of a particle may be prepared by the following procedure: (a) the particles are suspended in a liquid epoxy resin that contains a hardening accelerator; (b) the epoxy is allowed to harden and encase the particles; and (c) a microtome is used to prepare a thin section of the hardened epoxy. A thin section prepared in this manner will contain numerous thin sections of particles trapped within the hardened epoxy. The particle thin sections may represent only the tip of some particles and the center of other particles, depending on where the microtome happens to penetrate each individual particle. A particle thin section that represents a region near the center of the particle should contain a cross section of the structure inside the particle. In viewing such a thin section under the TEM, the solid areas appear black and the open areas associated with internal porosity or "pores" appear white. Thus, it is possible to obtain a cross-sectional view of the internal structure of the particle. Photomicrographs of these cross sections can, in principal, be used to gain qualitative information concerning the nature of the internal porosity, the relative amount of porosity, and the size of the pores. The thin sectioning procedure was attempted with a calcine produced by injecting Vicron limestone (>97% calcium carbonate) through the burner of a pilot-scale gas-fired combustor. Numerous attempts with various epoxy resins proved fruitless because the microtome could not be forced through the calcine particles without shattering them into many small fragments. The resulting fragmentation is illustrated in Figure 14. These fragments represent the remains of part of a calcine particle that was estimated to be roughly 10-20 µm in size originally. It is apparent that the thin section TEM procedure can be useful only if a nondestructive method can be devised for preparing the thin sections. This may be possible by cutting thicker sections and then milling them down using an ion beam.

MEASUREMENT TECHNIQUES

Energy Dispersive X-Ray (EDX) Analysis

Energy dispersive X-ray (EDX) analysis (6) can be used in conjunction with SEM to study the chemical composition of a small area (roughly 1 µm x 1 µm) within a field of particles. A beam of electrons is focused on the area of interest and this produces a spectrum of X-rays which are analyzed with respect to their intensities and wavelengths. The results are displayed as a spectrum of relative intensity, which is indirectly related to elemental concentration, as a function of the energy (keV) associated with the X-ray emissions from a given element. Thus, the location of a given peak in the spectrum identifies the element, and the peak height, after correction for that element, determines its relative abundance in the area analyzed. Figure 15 shows an example of two EDX spectra obtained on different areas of a fly ash/sulfated calcine mixture. Spectrum 28 suggests that the ~7-µm sphere in the top center is a fly ash particle, while Spectrum 29 shows that the mass in the lower left corner is mostly sorbent material. This illustrates how EDX can be used with SEM to identify various particle types and investigate their relative compositions. EDX can also be used to "map out" the areas in which a given element is concentrated within a given field of view. In this mode of operation, a microcomputer averages the "signals" received from various portions of the field of view over a period of time, and then displays the time-averaged result as a "dot map" of intensity as a function of location for a given element. This allows the operator to spot regions in which an element of interest is concentrated. The result of this procedure is illustrated in Figure 16, which shows the "dot maps" obtained for calcium, sulfur, and aluminum in a fly ash/sulfated calcine mixture. In this case, these maps show that the irregular particles in the lower portion of the SEM photo are sorbent particles while the smooth, spherical particles are fly ash.

Electron Microprobe Analysis

In electron microprobe analysis (EMA) a small area of the field of view is bombarded with a focused beam of electrons that is about 1 μm in diameter. This causes the sample area being analyzed to emit X-rays that are analyzed in terms of their diffraction by a known crystal lattice in the detector. The emitted X-rays emanate from as deep as 4-5 μm beneath the surface being analyzed (7). Therefore, the result is an average composition for the top 4-5 μm of the analysis area. The electron microprobe is normally used in a scanning mode to traverse across an area, or a single particle, of interest at a programmed rate. A microcomputer is used to convert the signal from the X-ray crystal analyzer and the programmed scan rate into a relative intensity profile across the area analyzed. The emitted X-ray signal for a selected element is monitored during a scan or traverse, and the scan is then repeated successively for every other element of interest. This results in a series of elemental profiles of the form illustrated in Figure 17. These profiles were obtained by scanning across a 30-μm area of sulfated sorbent material in a fly ash/sulfated calcine mixture. These profiles suggest more-or-less uniform sulfation across this particular region of the sulfated sorbent material. This apparent uniformity may be partially due to the effect of averaging over the top 4-5 μm of the area analyzed.

The results depicted in Figure 17 were obtained on a sample that had been imbedded in an epoxy resin. The hardened epoxy was metallographically polished to eliminate topographical effects in the EMA. The polishing may, however, tend to "smear out" the material and make it appear more uniform than it actually is. This could explain the apparent uniformity illustrated in Figure 17.

Electron Spectroscopy for Chemical Analysis (ESCA)

In the ESCA technique (8) a sample is pressed into a metal foil (e.g., indium) and irradiated with soft (1.25-1.49 keV) X-rays. Photoelectrons ejected from the core levels of surface molecules (top 10 Å) are analyzed with respect to their kinetic energy. The binding energy associated with the photoelectron peak is determined from the X-ray excitation energy, with the binding energy of the core level photoelectron being characteristic of the atom from which it originated. Chemical bonding information can be deduced by noting the precise positions and shapes of the ESCA peaks. The technique can be also used in conjunction with ion milling to obtain depth profile analyses.

The ESCA method typically analyzes an area of approximately 0.5 x 0.5 mm so that its single-particle capability is limited to material of this size or larger. Alternatively, the technique will provide an average surface analysis of many smaller particles when that type of information is satisfactory; although, in light of the purposes stated earlier in this paper, the lack of spatial resolution must be regarded as a shortcoming.

Auger Electron Spectroscopy (AES)

For the purpose of AES analysis (9), the sample is pressed into a metal (e.g., indium) foil and excited by a focused electron beam. A core level electron is ejected and replaced by an outer shell electron leaving the atom in an excited state. This excess energy is released by the ejection of a third electron called an Auger electron, which has an escape depth of about 10 Å. The characteristic kinetic energy of the Auger electrons is then analyzed to determine the relative intensities of the elements present. The analysis area for this technique is on the order of 1 μm^2 so it is suitable for single particle analysis of the small particles of interest in this study. AES, like ESCA, can be used in conjunction with ion milling to provide analyses at varying depths.

Table 2 shows the results of AES analyses performed in conjunction with argon ion milling for two samples believed to contain ash/sorbent interaction products and sulfated sorbent particles. Sample 0280-105 was produced by the burner injection of Vicron limestone sorbent while firing a 2% sulfur Indiana coal. Sample 0494-2 was produced by burner injection of Vicron limestone sorbent and kaolin while firing with H_2S-doped natural gas. Both analyses were produced on single particles approximately 10 μm in size. While sample 0494-2 shows no significant elemental changes down to 700 Å, sample 0280-105 appears to show an increase in aluminum and a decrease in calcium content with depth down to 900 Å. For particles in the 10-μm range, analysis depths of 900 Å still represent only the outer skin of the material. Further milling would be required to determine if a true layered structure were present in the particle. These results do indicate, however, the potential applicability of this technique to ash/sorbent interaction products.

CONCLUSIONS AND RECOMMENDATIONS

The results of this study have shown how selected visualization techniques (SEM and TEM) and selected measurement techniques (EDX, EMA, ESCA, and AES) can be applied to the characterization of LIMB-related samples. The SEM is particularly useful in elucidating the surface morphology of calcines and sulfated calcines. Surface features as small as 100 Å in size can be studied under a research-grade SEM. This was confirmed by high-resolution SEM photomicrographs of laboratory calcines that revealed slits on the order of this size. Information about the directional nature of the calcination process can also be inferred from SEM photomicrographs. The use of carbon replication TEM does not seem warranted in view of the good results obtainable by SEM and the problems associated with the preparation of carbon replicas. Thin section TEM may be a useful method for studying the internal structure of calcines and sulfated calcines if a nondestructive technique can be developed for the preparation of the thin sections. Ion milling may be one possible method of preparing the thin sections.

Energy dispersive X-ray (EDX) analysis may be employed in conjunction with SEM to chemically characterize particles or groups of particles observed under the SEM. The relative abundance of various elements in different samples may be estimated by comparison of the relative corrected peak heights, and the distribution of a given element within a field of particles can be determined from "dot maps" prepared by computerized analysis of the EDX signals. This technique is quite useful and easy to use. Electron microprobe analysis (EMA) can be used to study variations in elemental intensities across a region of a sample. However, it should be noted that the EMA results represent an average of the top 4-5 μm of the sample, so EMA is not appropriate for analysis of very small particles (<20 μm). Also, a metallographically polished section must be used to eliminate topographical effects, and the polishing can smear out the various chemical components near the polished surface.

Electron spectroscopy for chemical analysis (ESCA) is not appropriate for heterogeneous mixtures of fine particles (<500 μm) due to the poor spatial resolution. Even with a chemically homogeneous mixture of different particle sizes, it may be difficult to interpret the results of ESCA when employed with ion milling for depth profiling. For example, an etch depth of 1000 Å would result in an analysis of the center of a 0.2-μm particle and only the top 0.5% of a 20-μm particle. Thus, the result may represent a gross average of large particle surface compositions and small particle bulk compositions. Therefore, depth profiling must be done by the combination of Auger electron spectroscopy (AES) and ion milling, or by the direct method of secondary ion mass spectrometry (SIMS). The latter technique was not addressed in this study but appears to be a more straightforward method for depth profile analysis since the sputtered ions of the sample are analyzed directly during the milling process (10). Since AES is highly sensitive to particle charging effects and surface topography it is believed that SIMS analysis of individual particles may offer a better method of determining the depth of sulfur penetration into sulfated sorbent materials. It may also be useful in studies of ash/sorbent interaction products.

Some future effort will be directed toward the application of SEM, SEM/EDX, thin section TEM, and SIMS to the characterization of LIMB particulates. If possible, the SEM and thin-section TEM results will be related to conventional pore sizing by mercury intrusion or inert gas adsorption. It may be useful to relate the individual particle analyses obtained by SIMS to the analyses of larger areas by EDX and to bulk analyses that are obtainable by a variety of well-established techniques.

ACKNOWLEDGMENTS

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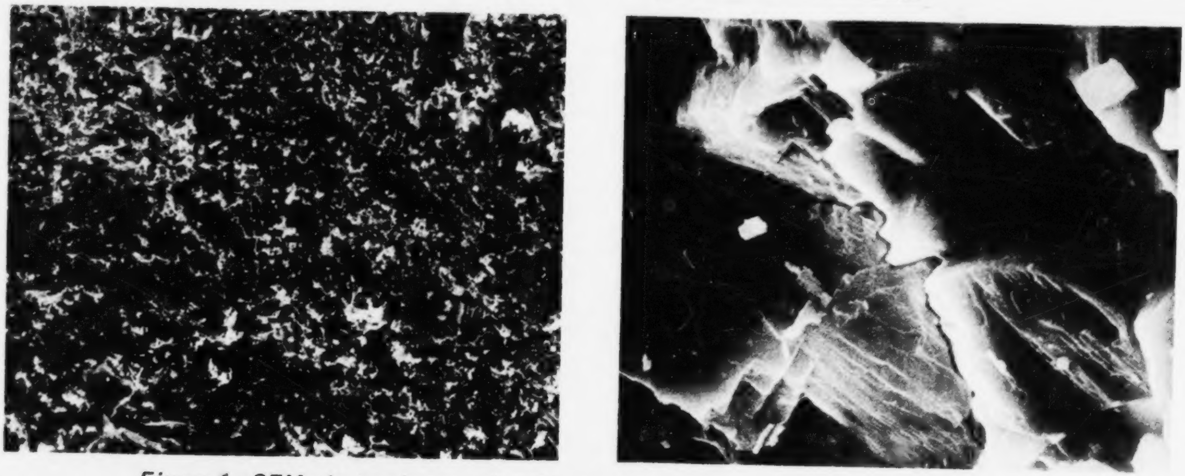


Figure 1. SEM photomicrographs of Longview stone chip at 100X and 2000X.

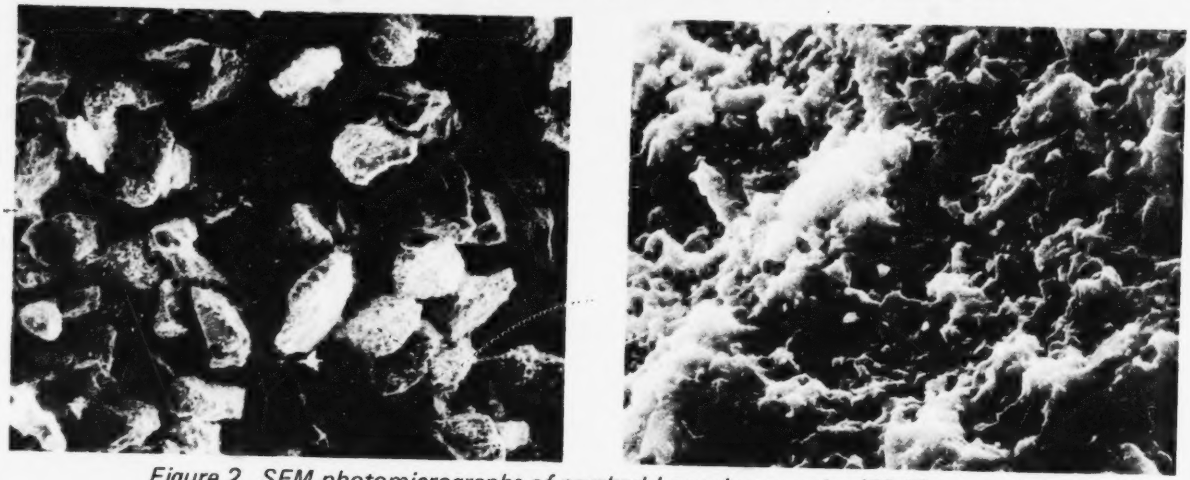
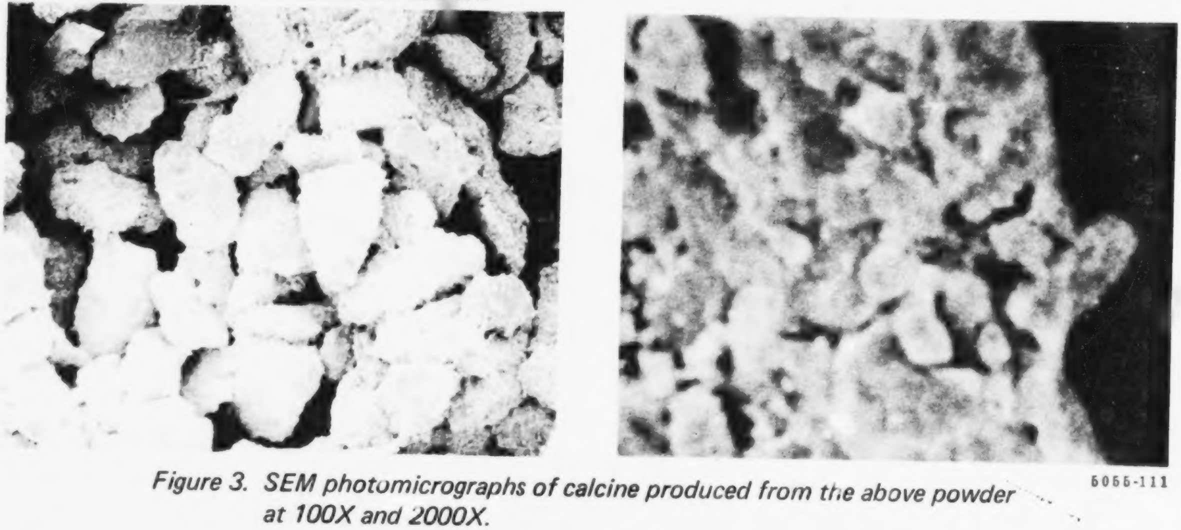


Figure 2. SEM photomicrographs of crushed Longview powder (63-58 μm cut) at 100X and 2000X.



5055-111

Figure 3. SEM photomicrographs of calcine produced from the above powder at 100X and 2000X.

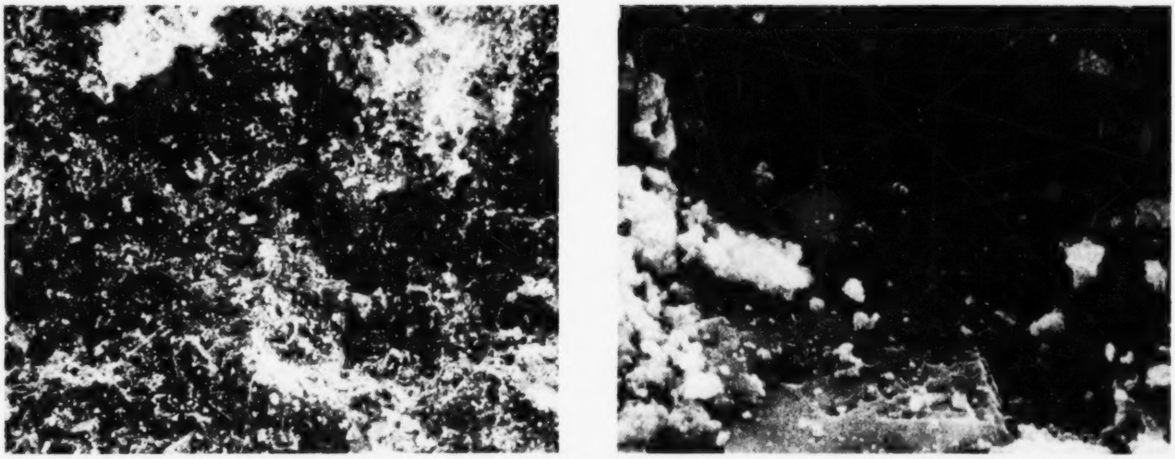


Figure 4. SEM photomicrographs of Maysville stone chip at 100X and 2000X.

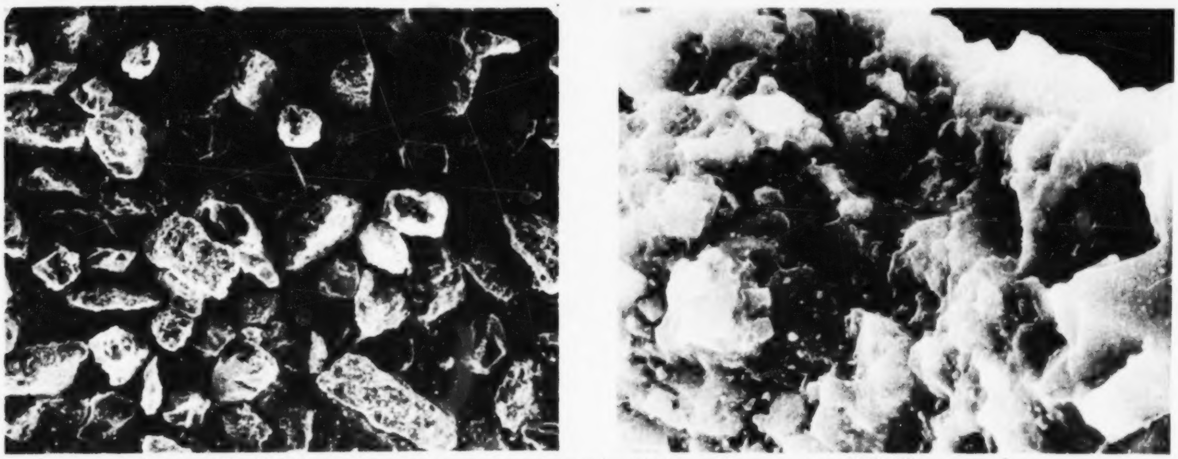
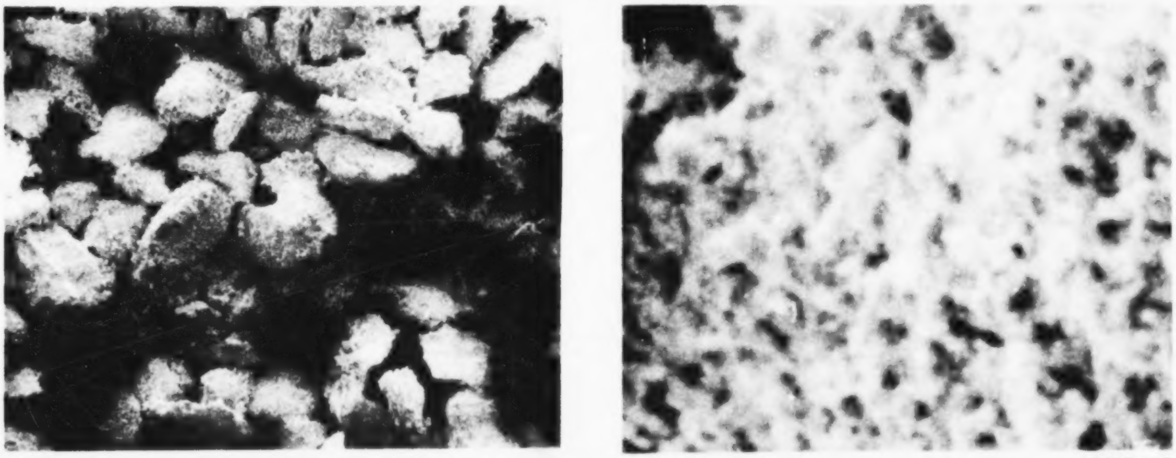


Figure 5. SEM photomicrographs of crushed Maysville powder (63-88 μm cut) at 100X and 2000X.



5055-112

Figure 6. SEM photomicrographs of calcine produced from the above powder at 100X and 2000X.

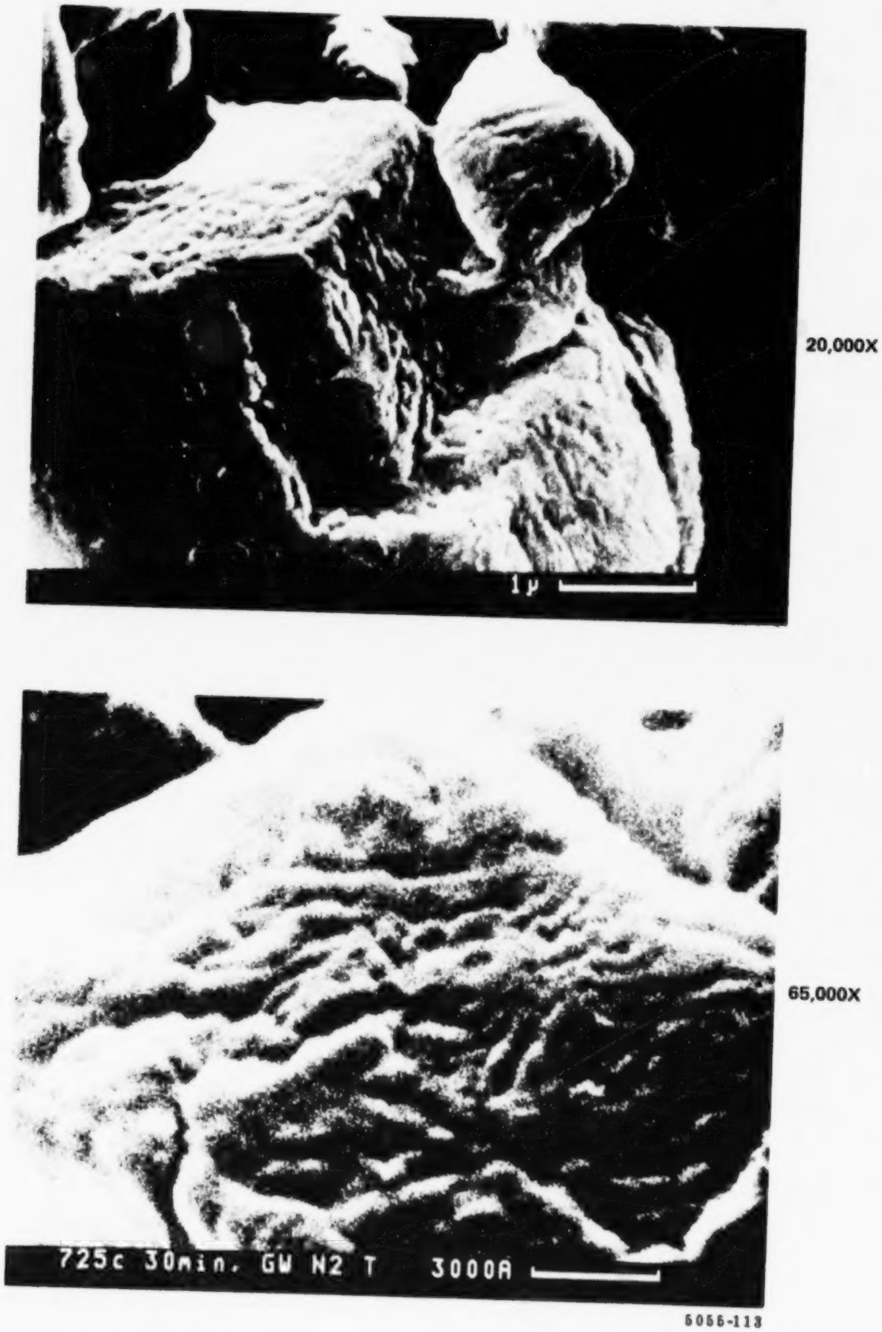

1μ
20,000X
65,000X
725c 30min. GW N2 T 3000A
5055-113

Figure 7. High-resolution SEM photos showing calcine surface morphology.

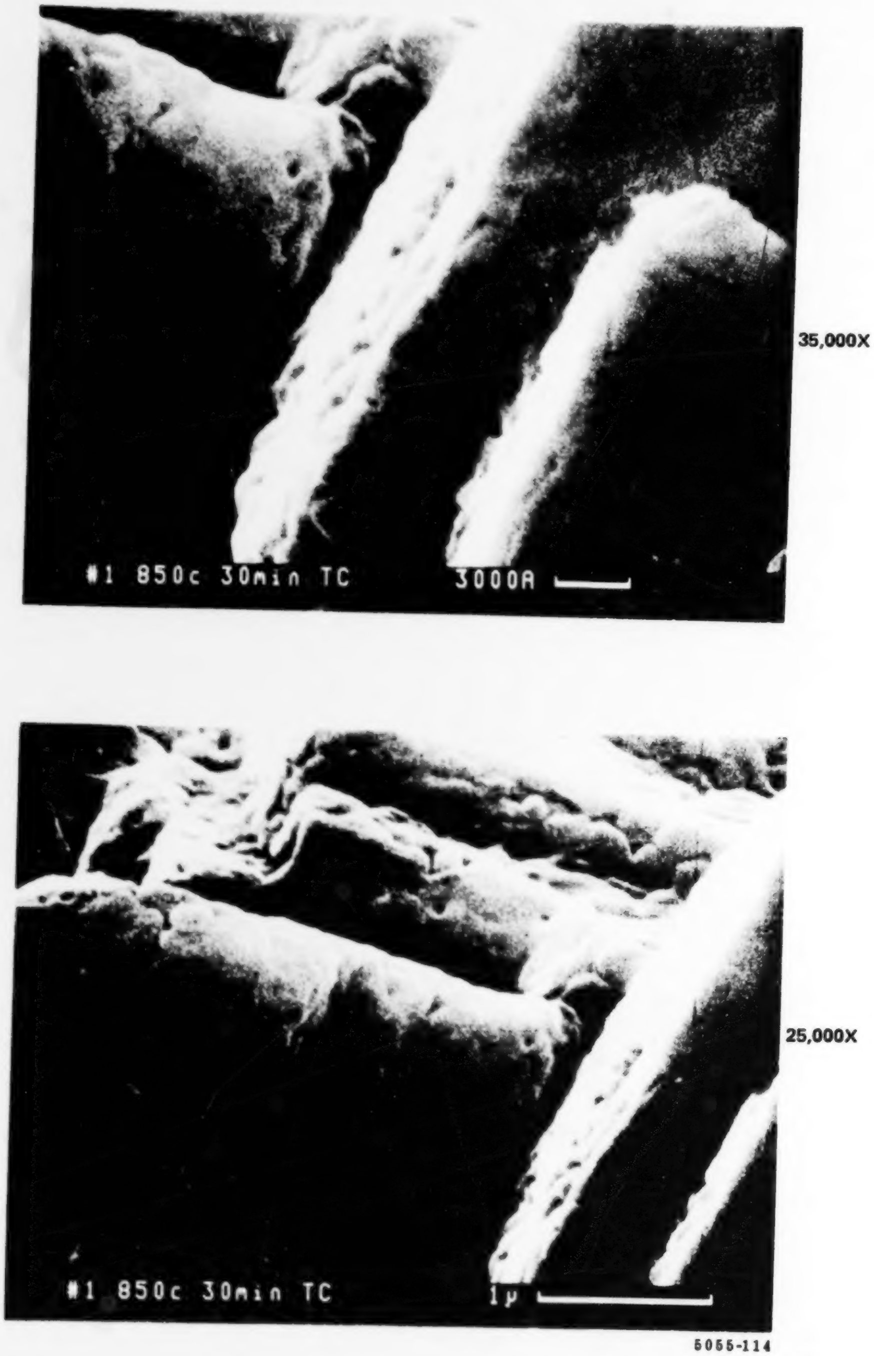

#1 850c 30min TC
3000A
35,000X
#1 850c 30min TC
1μ
25,000X
5055-114

Figure 8. SEM photomicrographs showing the directional nature of the calcination process and the fissure-like pore structure.

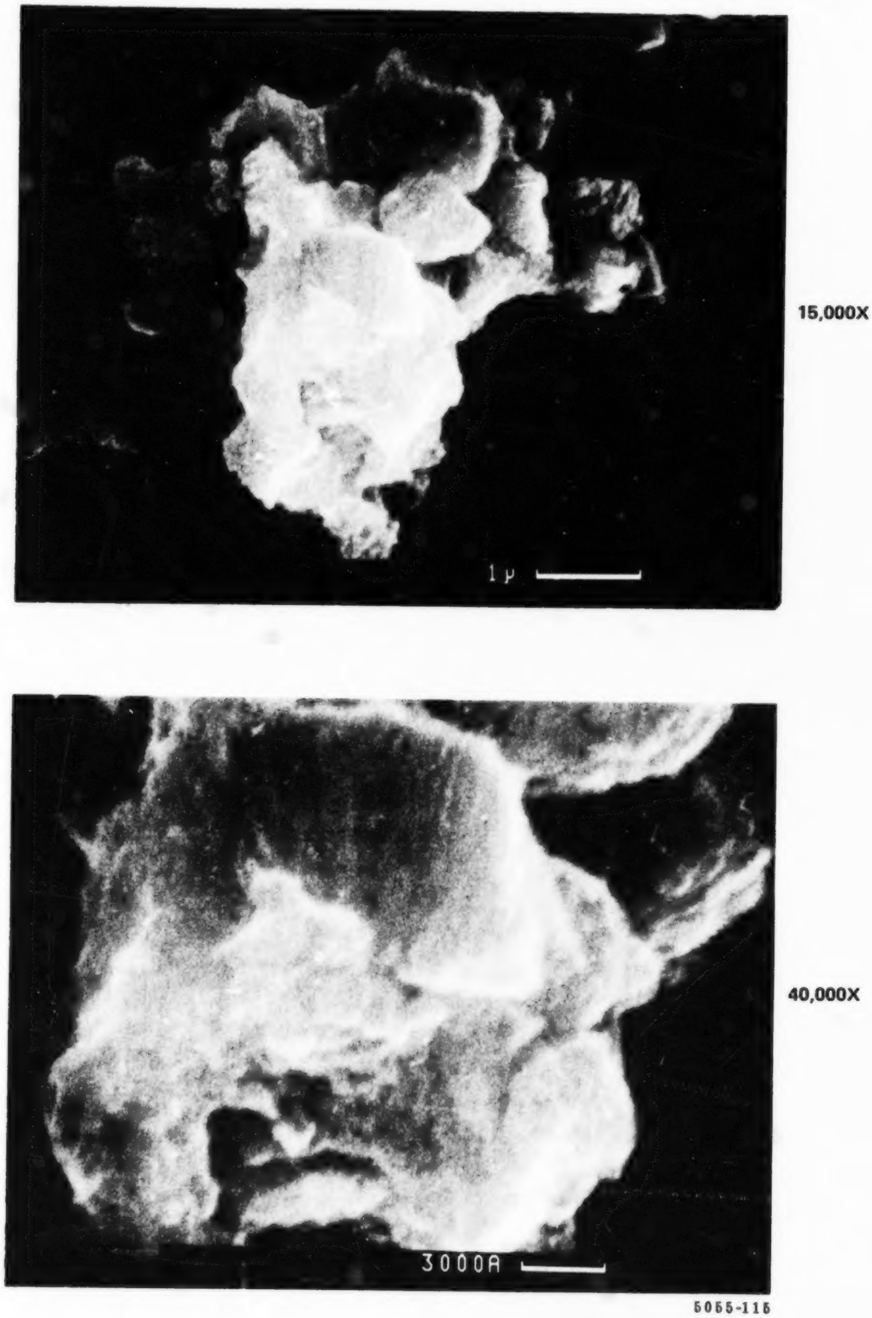

15,000X
1 μ
40,000X
3000A
5055-115

Figure 9. SEM photomicrographs of hydrated lime particles produced from Longview limestone.

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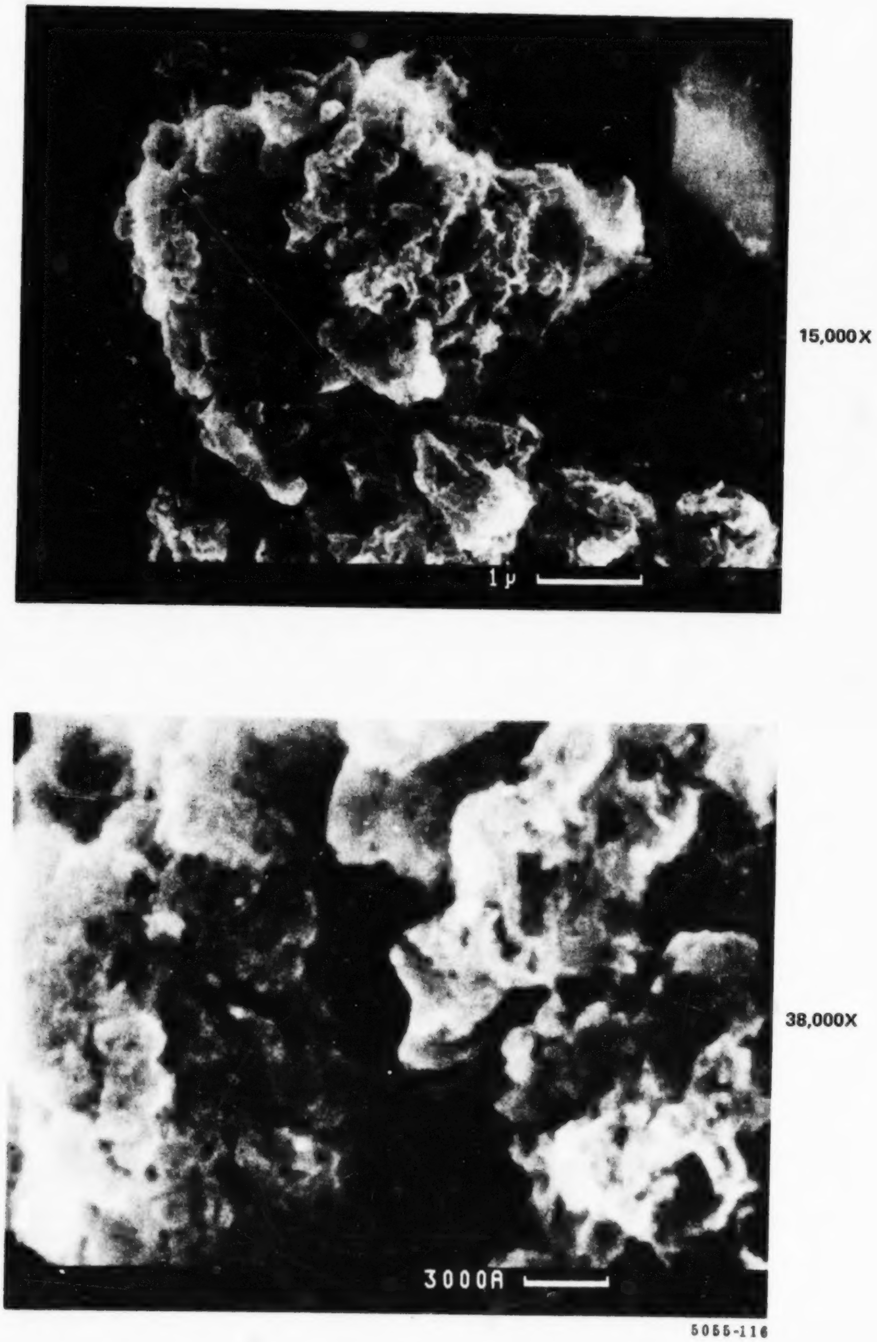

15,000X
1µ
38,000X
3000Å
5055-116

Figure 10. SEM photomicrographs of calcine particles produced from hydrated lime.

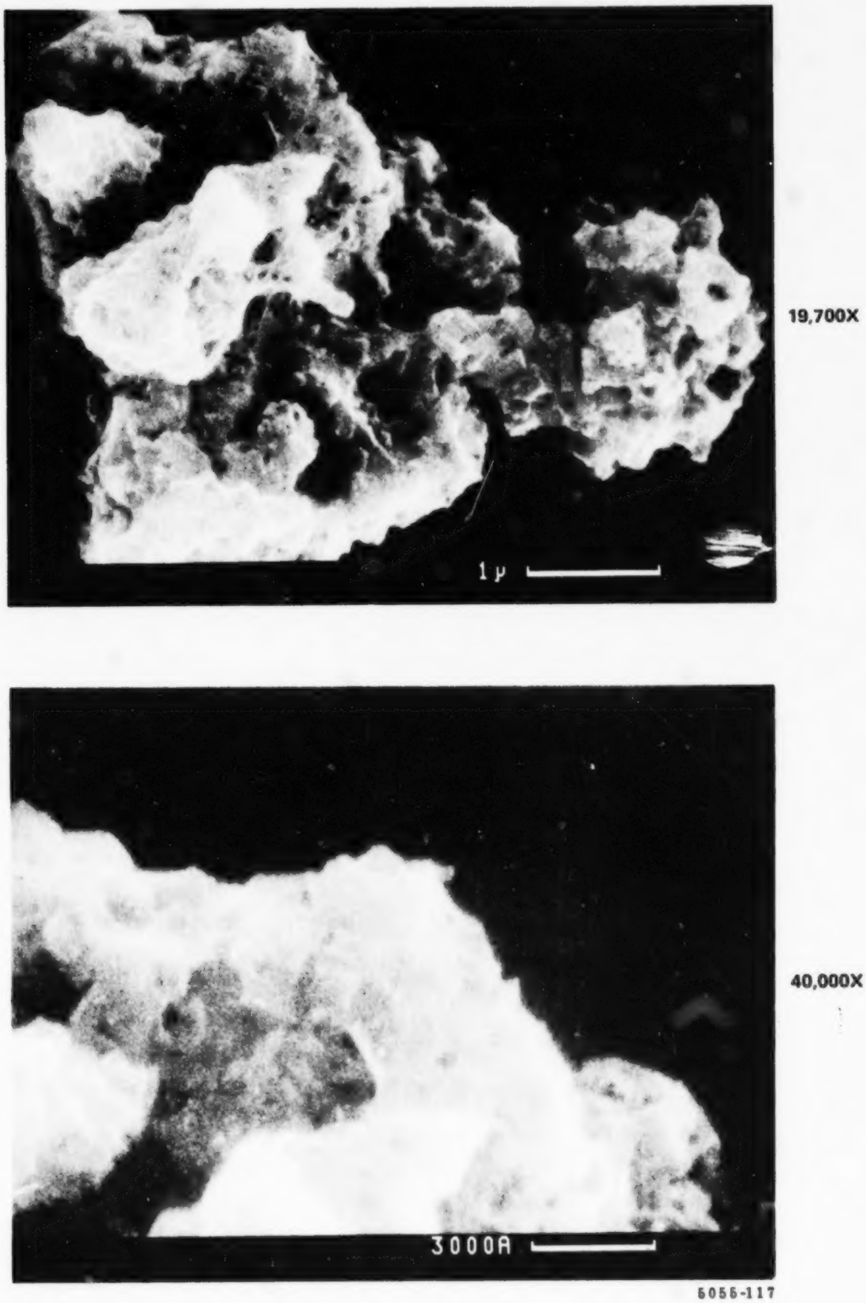

19,700X
1μ
40,000X
3000Å
5055-117

Figure 11. SEM photomicrographs of sulfated calcine particles produced from hydrate.

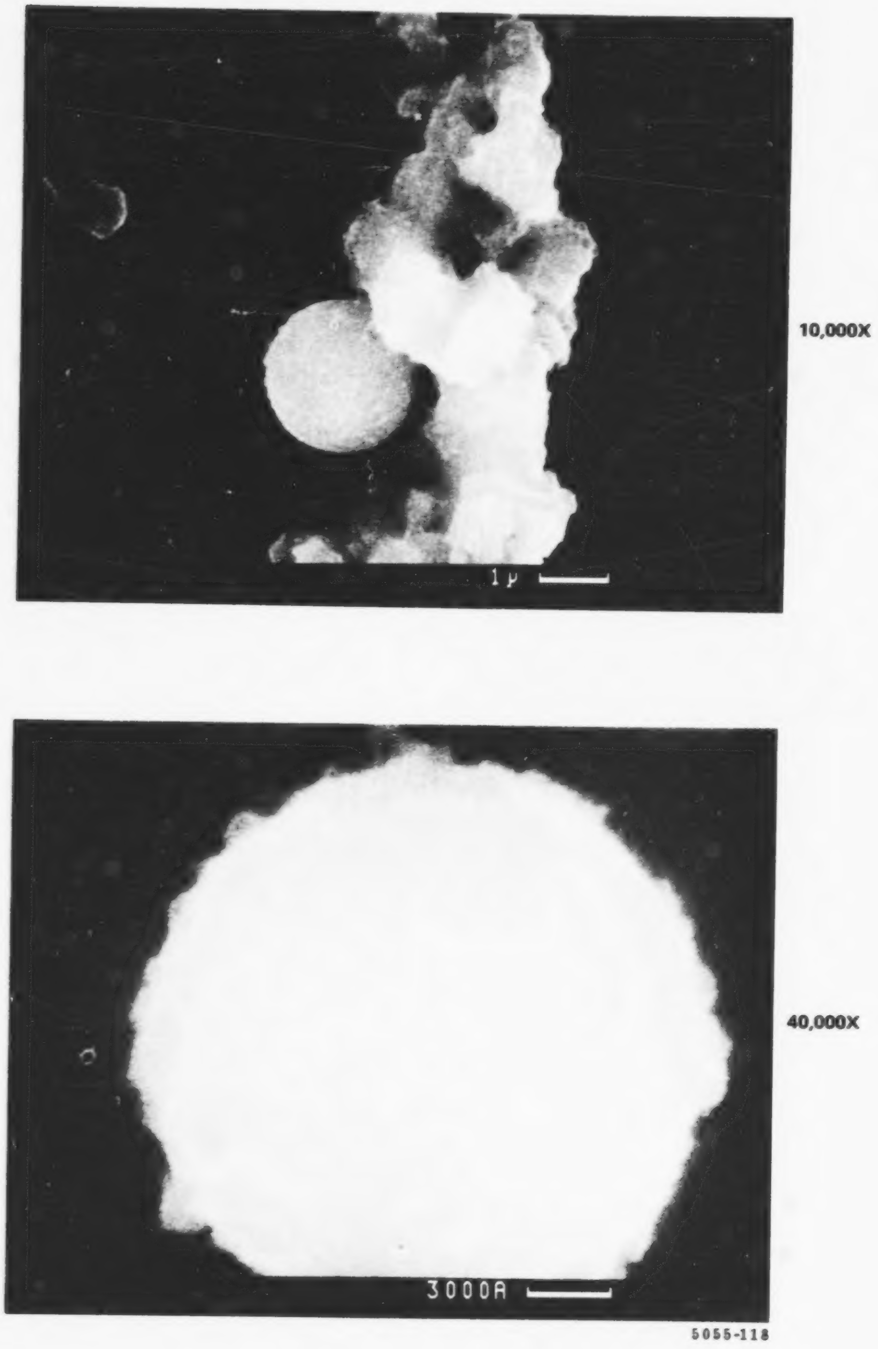
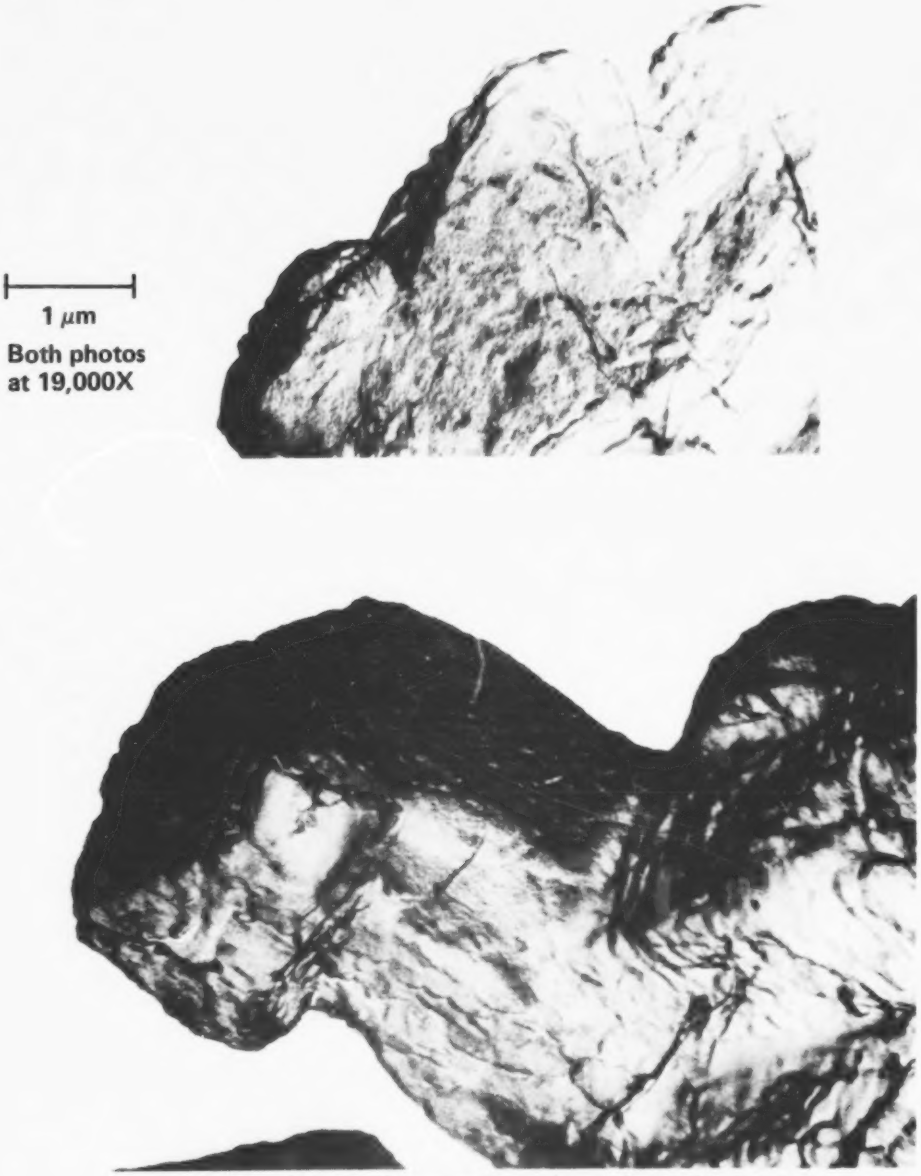

1μ
10,000X
3000Å
40,000X
5055-118

Figure 12. SEM photomicrographs of sulfated calcine particles in combination with fly ash from a medium-sulfur coal.


1 μm
Both photos at 19,000X

a. Produced by heating reagent-grade calcite for 30 minutes at 850 °C in static air environment.

5055-119

Figure 13. Carbon replica of calcined limestone particles[a].

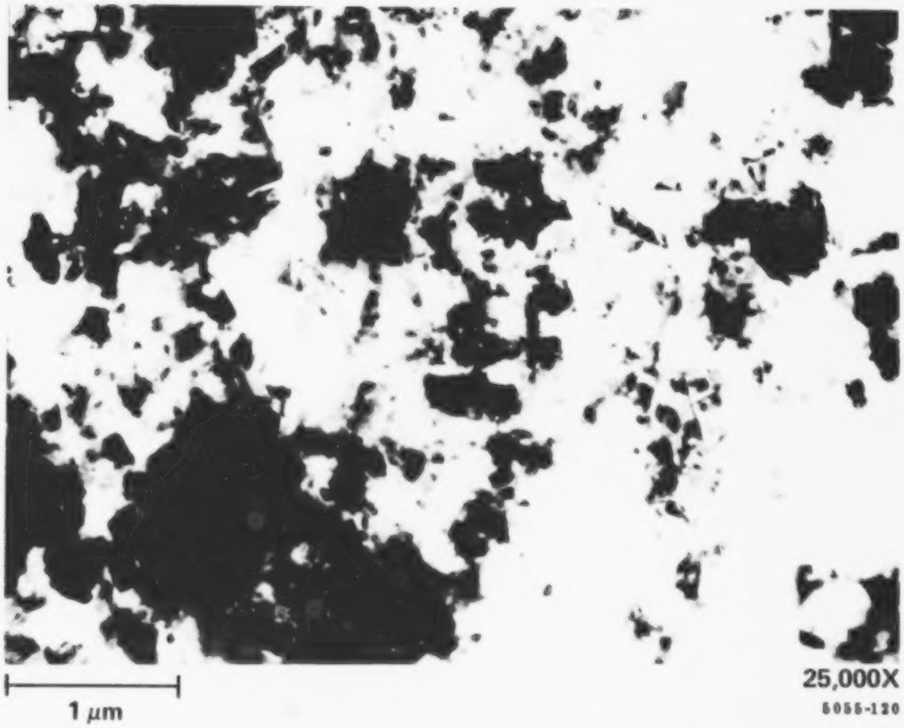

1 μm
25,000X
5055-120

Figure 14. Thin section containing fragments of calcined Vicron particle taken from SRI combustor.

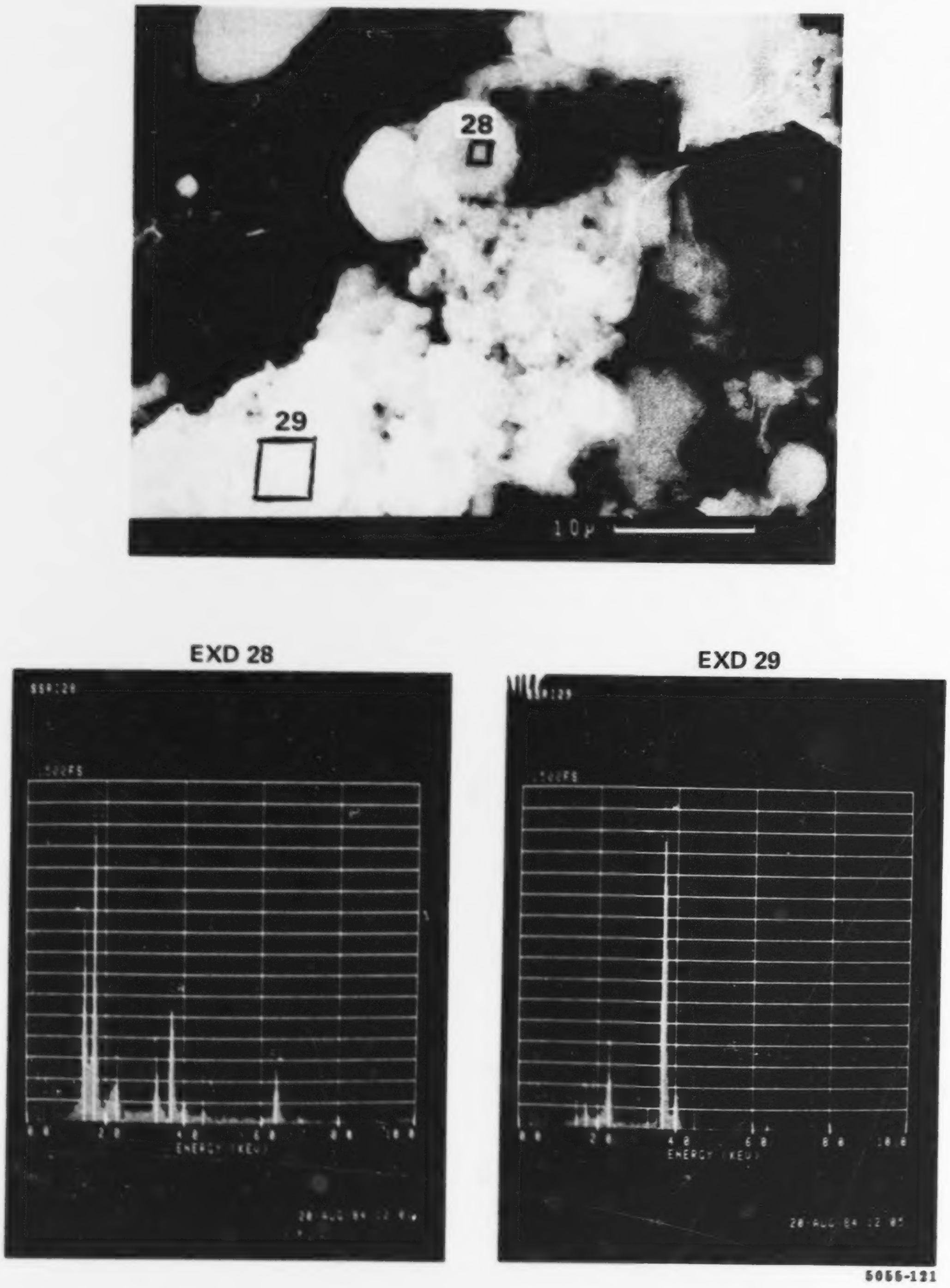


Figure 15. EDX spectra obtained on two different areas of a fly ash/sulfated calcine mixture.

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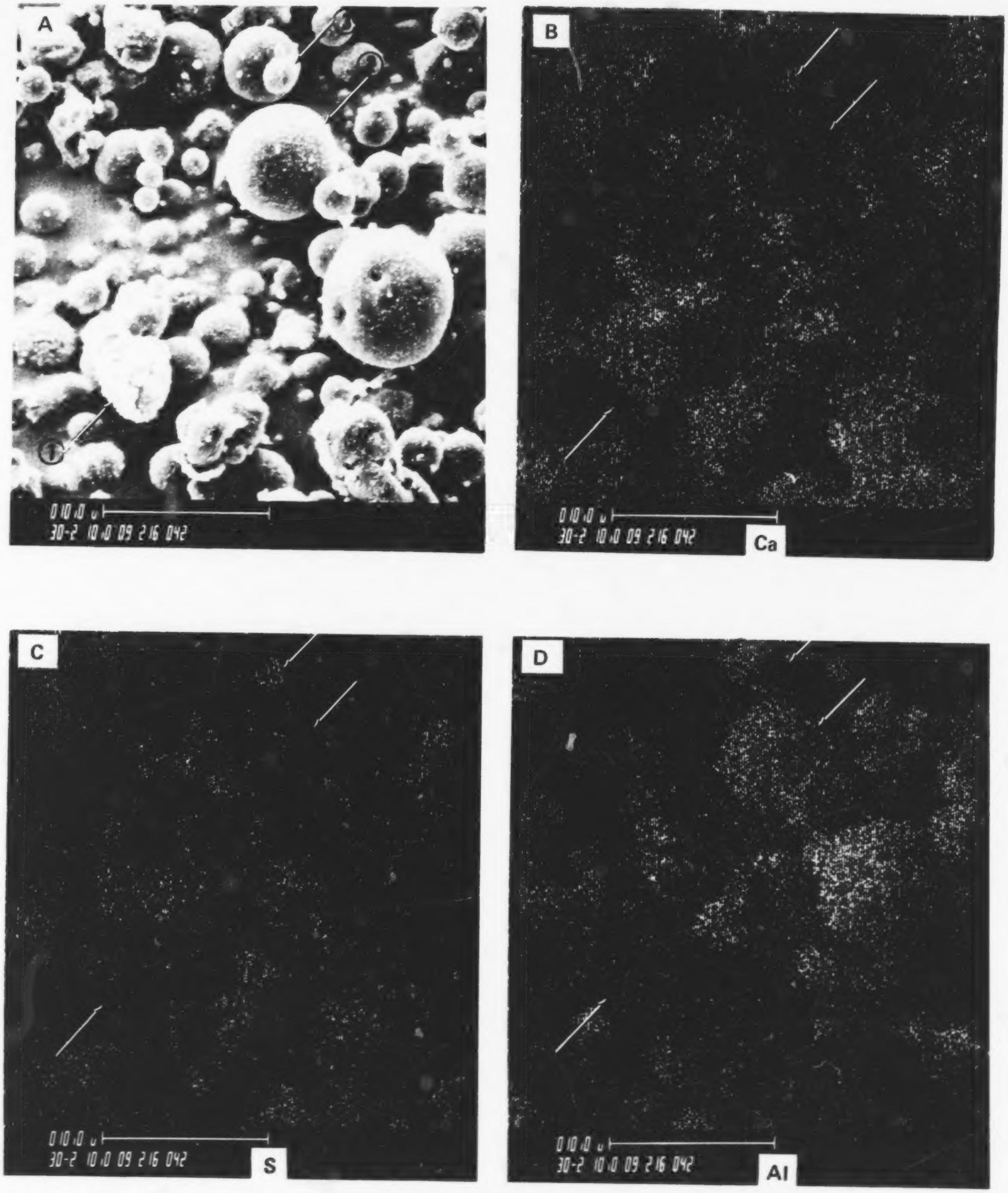
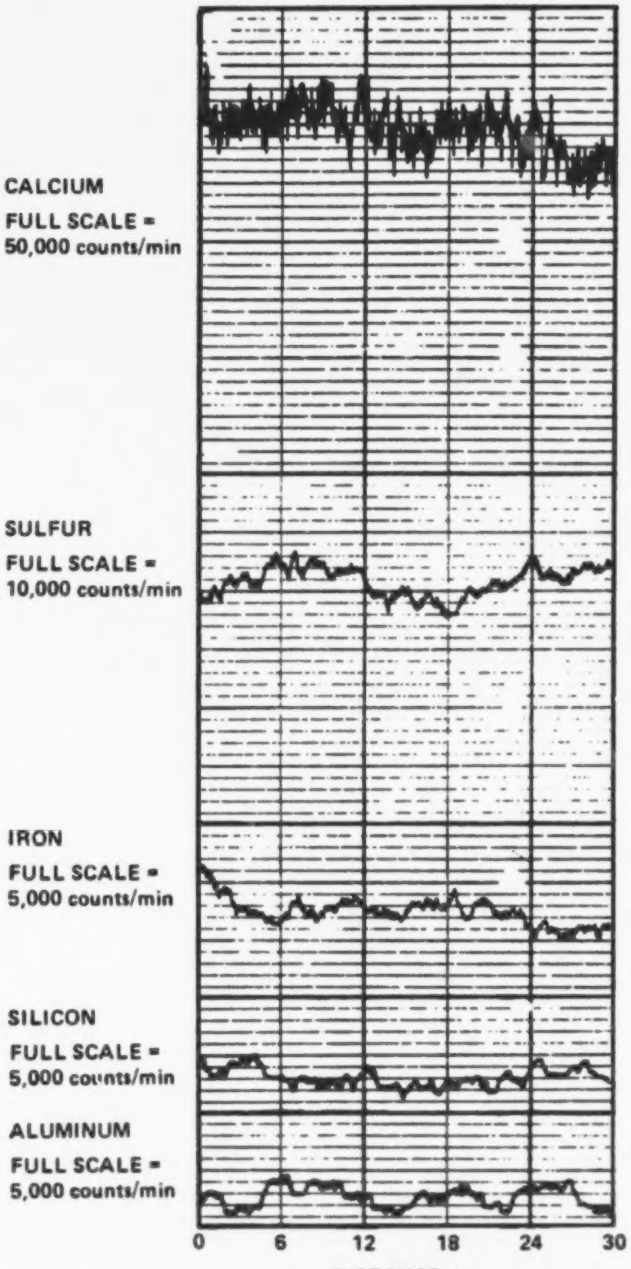

A
B
C
D
1
Ca
S
Al
0 10 10 u
30-2 10 10 09 216 042

5055-54

Figure 16. EDX maps of calcium, sulfur, and aluminum in a fly ash/sulfated calcine mixture.



a. Natural gas doped with 2270 ppm SO_2; capture = 22%

5055-122

Figure 17. Electron microprobe scans across a sulfated calcine particle produced by burner injection of Vicron limestone in a pilot-scale combustor.

Table 1

LIMESTONES EXAMINED BY SEM

Name Supplier Quarry Location	Longview Southern Industries Saginaw, AL	Maysville Dravo Lime Co. Maysville, KY
% Loss on ignition	43.4	43.5
% $CaCO_3$	96.6	91.4
% $MgCO_3$	1.9	5.8
% SiO_2	0.54	1.5
% Al_2O_3	0.68	0.68
% Fe_2O_3	0.17	0.21
% K_2O	0.03	0.11
% SO_3	0.15	0.22

Table 2

DEPTH PROFILES DETERMINED BY AES WITH ION MILLING

Etch Depth (A)	% Si	% Al	% O	% Ca	% S
	0280-105 Ash/sorbent mixture				
0	4.3	2.5	34	47	5.4
300	5.2	10	33	34	9.7
900	3.1	13	37	35	5.5
	0494-2 Kaolin/sorbent mixture				
0	3.3	5.5	37	48	1.6
25	4.0	7.2	36	45	1.6
100	3.5	8.2	39	48	1.9
700	3.3	6.6	36	53	0.9

APPENDIX A
LIST OF ATTENDEES

1ST JOINT SYMPOSIUM ON DRY SO_2 AND SIMULTANEOUS SO_2/NO_x CONTROL TECHNOLOGIES
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